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# CONTENTS

303

# IV  VEHICLES AND FUELS

# Effect of E85 fuel on performance parameters, fuel consumption and engine efficiency – Škoda Fabia 1.2 HTP

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**Abstract:** This article deals with the effect of the E85 fuel on the performance parameters, specific fuel consumption and engine efficiency of a spark ignition engine Škoda Fabia 1.2 HTP and it is related to the article Effect of E85 Fuel on Harmful Emissions – Škoda Fabia 1.2 HTP. The measurement was performed on a test bench using a test cycle that simulates real traffic conditions and simultaneously the external rotation speed characteristics were measured. Three variants were chosen for burning E85 fuel. The first one was the usage of the E85 fuel without modifications on the engine control unit (variant 1 – E85), the second one was the usage of the E85 fuel with prolonged time of the injection by 28% (variant 2 – E85+) and the last third variant was the reference fuel petrol Natural BA95 (variant 3 – N95) for comparison. The results of the measurement showed a non-negligible decrease of the engine torque and power for both variants using E85 fuel. Further, there was a considerable increase of the specific fuel consumption for variants 1 and 2 (E85, E85+). Engine efficiency for the driving cycle increased for variants 1 and 2 (E85, E85+) approximately by one percent. For the external rotation speed characteristics the engine efficiency increased approximately by 5% for variant 1 – E85 and approximately by 2% for variant 2 – E85+.

**Key words:** E85 fuel, performance parameters, fuel consumption, engine efficiency.

## INTRODUCTION

The increase in the usage of bioethanol as a fuel in Europe is significant (up to 15% annually) (Beran, 2011). The reason could be the European Parliament and the European Council, which adopted the so called action plan concerning with the issue of biofuels in transport. In the action plan the strategy for achieving the planned 20% substitution of conventional liquid motor fuels with alternative fuels by 2020 is defined (Šebor et al., 2006). Furthermore according to the European Directive 2009/28/EC on the promotion of the use of energy from renewable sources and amending and subsequent repealing directives 2001/77/EC and 2003/30/EC the target is a 20% share of energy from renewable sources and a 10% share of energy from renewable sources in transport (EU Directive 2009/28/EC; Hromádko et al., 2009; Beran, 2011; Pirs & Gailis, 2013). The second reason could be the dependence of Europe on the imported crude oil products. European OECD countries were dependant on the imported crude oil in the year 2007 from about 65% and by 2030 the dependence could increase up to 83%. The transport in Europe is dependant on the crude oil products from about 98% (Šebor et al., 2006; IEA, 2009; Gnansounou, 2010). France is the major consumer of

bioethanol in Europe with a 5.41% share of bioethanol on the market (in Sweden it is 5.14%) (Gnansounou, 2010).

The most used fuel with higher share of bioethanol is the E85 fuel, which is made from 85% bioethanol and from 15% petrol. In comparison with the petrol the E85 fuel has lower energy content and higher density, it also has higher share of oxygen and therefore lower stoichiometric ratio. Furthermore it has a higher heat of evaporation, lower Reid vapour pressure, higher octane number and therefore an option of using higher compression ratio than petrol (Pumphrey et al., 2000; da Silva et al., 2005; Laurin, 2006a; Laurin, 2006b; Šebor et al., 2006; Mužíková et al., 2010; Hromádko et al., 2011; Küüt, et al., 2011). Taking into account new technologies of its production (second and third generation bioethanol) it could be a perspective alternative fuel which reduces the content of released greenhouse gases and the dependence on the crude oil (Varga et al., 2003; Liu & Shena, 2008; Sánchez & Cardona, 2008; Hromádko et al., 2009; Goh & Lee, 2010; Hromádko et al., 2010).

There are 2 possible variants of the E85 fuel use in the spark ignition engine. The first one is the engine customized directly for using of E85 fuel. For this engine the compression ratio can be increased up to 15:1 because of high octane number of the E85 fuel (RON 110) (Laurin, 2006a; Laurin, 2006b). The second variant are the Flex-Fuel vehicles (FFV). These vehicles can be operated with any mixture of E85 fuel and petrol. FFVs are the most used in Brazil, from the European countries in Sweden. (Laurin, 2006a; Kamimura et al., 2008; de Melo et al., 2012).

The purpose of the experiment was to verify the effect of the E85 fuel on performance parameters of the engine, specific fuel consumption and engine efficiency. According to the other experiments in this field (Čupera & Polcar, 2011; Küüt et al., 2011; Vojtíšek-Lom & Mazač, 2011; de Melo, 2012; Pirs & Gailis, 2013) the following assumptions can be established. The engine torque and power will be lower due to unmodified engine, specific fuel consumption can be higher due to the lower energy content of the bioethanol share in the E85 fuel and the engine efficiency could be higher. For experiment the test cycle, which simulates real traffic conditions, was used. Furthermore, for detection of the maximal values and progression of the engine torque, power and specific fuel consumption, the external rotation speed characteristics were measured.

## MATERIALS AND METHODS

The whole experiment was performed on the test bench of the Department of Vehicles and Ground Transport at the CULS Prague.

For the experiment an electric-swirl dynamometer V125 with construction IP23/ICW37 was used. The reaction from the dynamometer was captured via a tensometric sensor with nominal load 2kN and merged mistake 0.5% of the nominal load.

The measurements were performed on the engine Škoda Fabia 1.2 HTP. This engine is a three-cylinder atmospheric in-line four stroke engine, it has overhead cams with 2 valves per cylinder. Max. power is 40 kW at 4,750 rpm, max. torque is 106 Nm at 3,000 rpm and the compression ratio is 10.3:1.

The measurements were performed for the following variants. The E85 fuel without modifications of the engine control unit (variant 1 – E85), E85 with prolonging

of the time of the injection (variant 2 – E85+) and Natural BA95 (variant 3 – N95). For prolonging of the time of the injection for the second mentioned variant an additional control unit plugged between ECU and injectors was used. That means that the input for this unit are the impulses for the injectors sent by ECU and the additional unit is extending them by preset period in percentage and is sending them to injectors. In the case of the variant 2 (E85+), the prolonging of the time of the injection was by 28%.

For communication with ECU the diagnostics system VAG-COM was used. This system was primary used for reading values from ECU, such as rotations, load of the engine (in percentage) and the air-fuel equivalence ratio.

The test cycle was acquired from real traffic by recording values from the OBD diagnostics system of the vehicle and the length of the cycle is 330 sec. The whole cycle is characterized by the dependence of the position of the gas pedal on the time of the driving cycle (Fig. 1). During the cycle the values of the torque and rotations of the engine are not the same for all variants of the used fuel (Figs 2 and 3). The reason are the different performance parameters of the engine as a result of different heating values of the used fuels.
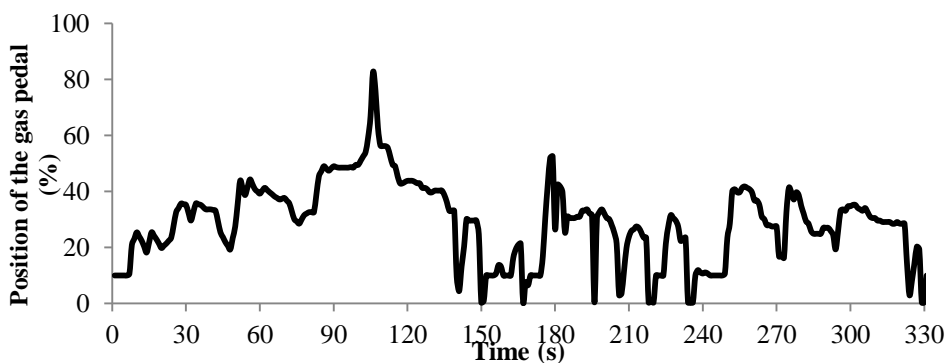


**Figure 1.** Progression of the position of the gas pedal during the test cycle.
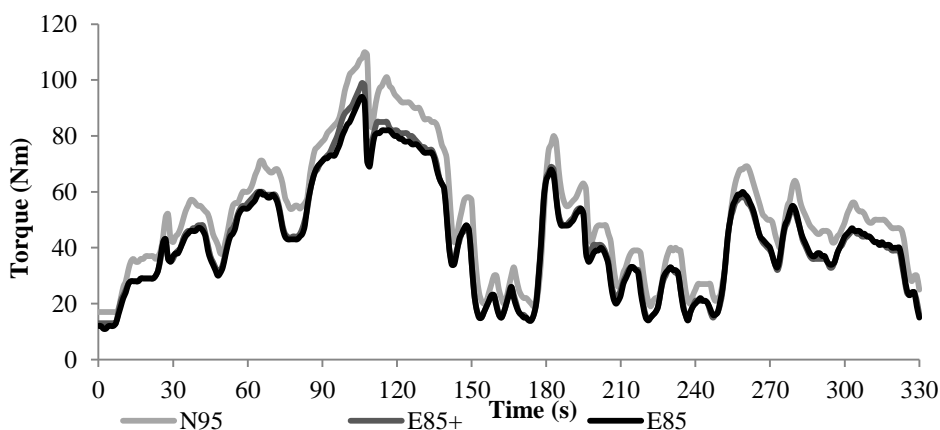


**Figure 2.** Progression of the torque during the test cycle.

Furthermore, on the above mentioned dynamometer the external rotation speed characteristics were measured for each variant of the used fuel. The position of the gas

pedal was on 100% and by increasing torque the rotations were decreased. In every predetermined measurement point the measured parameters were stabilized.
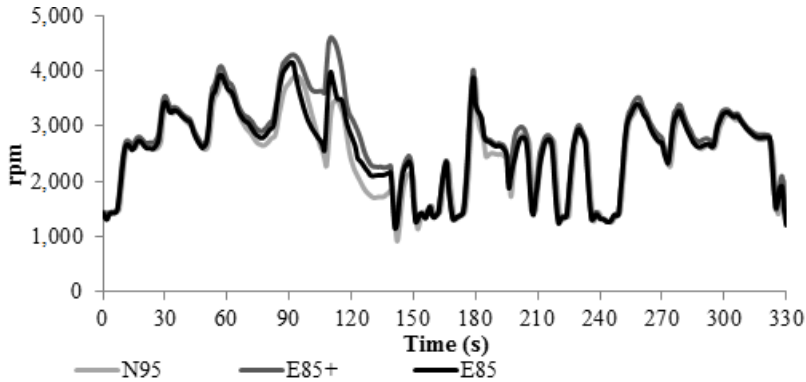


**Figure 3.** Progression of the rotations during the test cycle.

All measured parameters are logged with frequency of 1 Hz into a DBF file on the hard drive of the computer. These measured data were further processed using MS Excel.

## RESULTS

The fuel consumption was evaluated for the whole cycle cumulatively. For the driving cycle with variant 1 (E85) 469.2 g of fuel was consumed, with variant 2 (E85 +) 512.6 g of fuel was consumed and with variant 3 (N95) 380.1 g of fuel was consumed. From these data it is evident that with variant 1 and 2 the fuel consumption increased. With simultaneously decreased performance parameters of the combustion engine, the specific fuel consumption increased by 40%.

To be possible to express the engine efficiency, for each variant of the fuel the heating value and density was specified. The resulting values reached during the whole driving cycle are listed in Table 1.

The engine efficiency increased approximately by one percent. Specifically for variant 1 (E85) the efficiency increase is 1.1% and for variant 2 (E85+) the increase is 1.0%.

**Table 1.** Summarized results of the measuring using the driving cycle

| Variant | Specific fuel consumption (g kWh$^{-1}$) | (%) | Efficiency (%) |
|---------|------------------|-------|------------|
| E85     | 402              | 141.4 | 30.3       |
| E85+    | 404              | 142.2 | 30.2       |
| N95     | 284              | 100   | 29.2       |

The external rotation speed characteristics for each variant are showed gradually in Figs 4, 5 and 6.

In Fig. 4 the progression of the performance parameters and specific consumption of the engine with variant 1 (E85) is shown. Compared to variant 3 (N95) the decrease of maximal engine power by 10.7% and maximal torque by 7.8% and the increase of

310

the specific fuel consumption by 23.2% can be seen. The measurement of this variant always concluded with an error of the ECU, which was reporting too poor mixture, both in the case of the measurement of external rotation speed characteristic and in the case of the driving cycle.
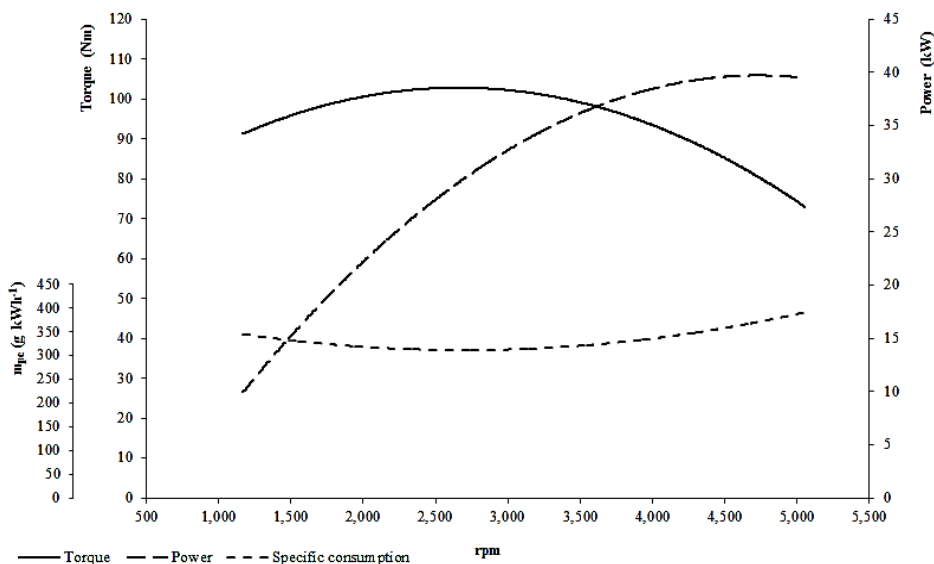


**Figure 4.** External rotation speed characteristic for variant 1 – E85.

In Fig. 5 the external rotation speed characteristic for variant 2 (E85+) is shown. Again, the decrease of the maximal engine torque (by 4.3%) and power (by 9.7%) can be seen, but not as significant as for the variant 1 (E85). If the negative effect of this variant on the emissions, described in the paper Effect of E85 Fuel on Harmful Emissions – Škoda Fabia 1.2 HTP, would be neglected, the engine was working properly. It is also confirmed by the fact, that after measuring this variant, the ECU was reporting no error message.

The external rotation speed characteristic for variant 3 (N95) is shown in Fig. 6. This variant was used as a reference one. Especially, significantly lower specific fuel consumption compared to the variants 1 and 2 (E85, E85+) can be seen.

During the measurement of the external rotation speed characteristics, both variants using E85 fuel (E85, E85+), showed a significant increase of the combustion engine efficiency compared with the variant 3 (N95). Variant 1 (E85) showed the highest engine efficiency, as expected. This can be explained, among others, by a poor mixture combusted in the cylinders. For variant 2 (E85+), where the mixture was richer than for variant 3 (N95), the better efficiency can be explained by a better combusting because bioethanol is a simpler hydrocarbon than the petrol, which is a mixture of hydrocarbons, therefore combusting E85 produces less intermediates. Furthermore, bioethanol contains significant share of oxygen (34.7%).

311
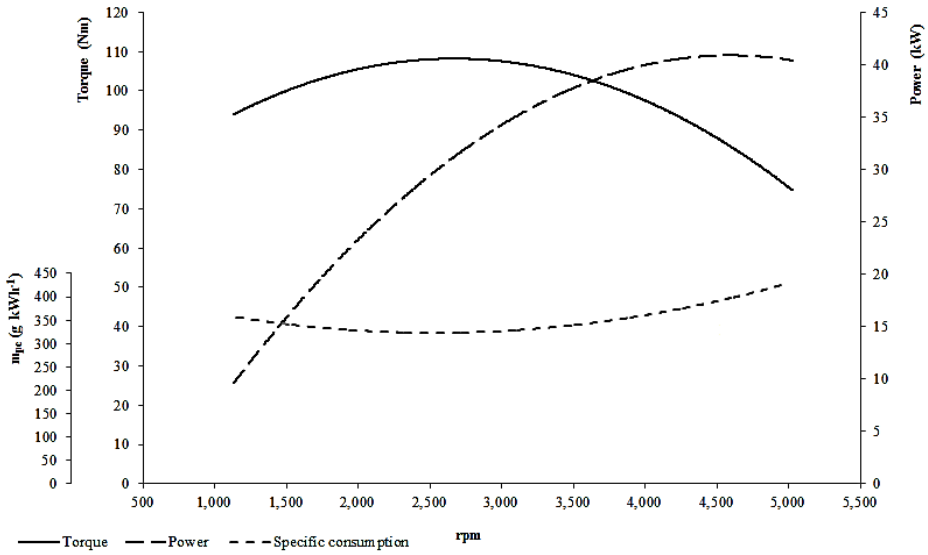
**Figure 5.** External rotation speed characteristic for variant 2 – E85+.
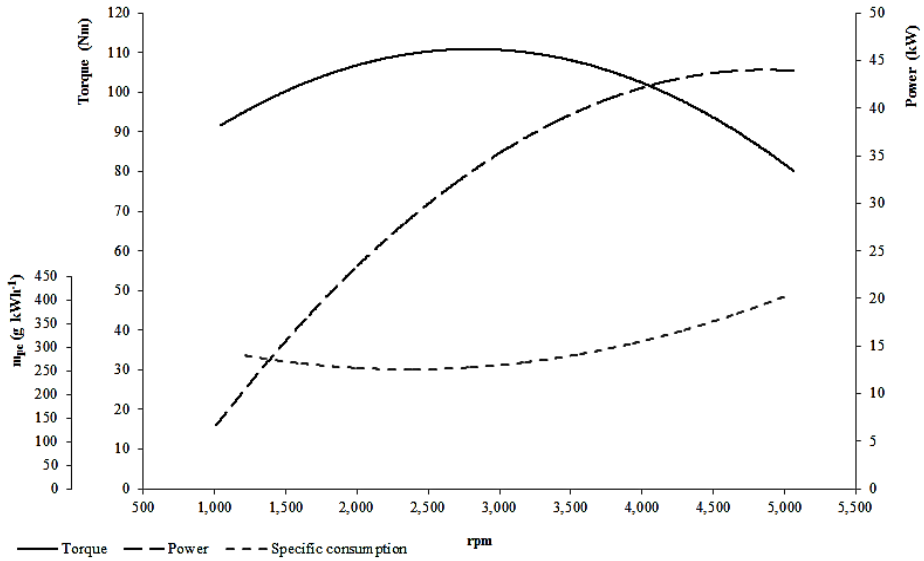


**Figure 6.** External rotation speed characteristic for variant 3 – N95.

**Table 2.** Summarized results of the external rotation speed characteristics

| Variant | Torque | | Power | | Specific fuel consumption | | Efficiency |
|---------|--------|-------|-------|-------|-----------------------------|----------|------------|
| | (Nm) | (%) | (kW) | (%) | (g kWh$^{-1}$) | (%) | (%) |
| E85 | 107 | 92.2 | 40.7 | 89.3 | 343 | 125.37 | 35.6 |
| E85+ | 111 | 95.7 | 41.2 | 90.4 | 379 | 138.41 | 32.2 |
| N95 | 116 | 100 | 45.6 | 100 | 274 | 100 | 30.4 |

In Table 2 it can be seen that for both variants using E85 (E85, E85+) the engine power decreased approximately by 10%. The torque decreased for variant 1 (E85) approximately by 8% and for variant 2 (E85+) approximately by 4%. Specific fuel consumption increased, as expected, for variant 1 (E85) approximately by 23.2% and for variant 2 approximately by 35.8% compared to the variant 3 (N95). The E85 fuel achieved success during evaluation of the engine efficiency. The engine efficiency increase by 5.2% for variant 1 (E85) and approximately by 1.8% for variant 2 (E85+) can be seen. In real traffic, probably, it would not be possible to reach these values. Furthermore, permanent operation of variant 1 (E85) is not possible because even after repeated measurements the ECU was reporting an error message indicating too poor mixture.

## CONCLUSION

From the viewpoint of the measurements using the driving cycle it can be claimed that the use of the E85 fuel brings the specific fuel consumption increase approximately by 40% (variant 1 – E85 by 41.1%, variant 2 – E85+ by 42.2%) compared with variant 3 (N95). But the engine efficiency increased by cca 1% (variant 1 – E85 by 1.1%, variant 2 – E85+ by 1.0%).

As can be seen in Table 2, for both variants using E85 (E85, E85+) the engine power decreased approximately by 10%. Specific fuel consumption increased, as expected, for variant 1 (E85) approximately by 23.2% and for variant 2 approximately by 35.8% compared to the variant 3 (N95). The E85 fuel achieved success during evaluation of the engine efficiency. The engine efficiency increase by 5.2% for variant 1 (E85) and approximately by 1.8% for variant 2 (E85+) can be seen.

To conclude, despite the weaknesses of the E85 fuel, such as aggressivity on the sealing elements and lower performance parameters, it is possible that in this fuel a key to the future can be. It can be combusted with a relatively small interference in the fuel system of the combustion engine (mainly prolonging of the time of the injection) and by usage of this fuel the better combusting efficiency can be achieved.

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# Effect of E85 Fuel on Harmful Emissions –
# Škoda Fabia 1.2 HTP

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**Abstract:** This article deals with harmful emissions production by a spark ignition engine Škoda Fabia 1.2 HTP operating on E85 fuel. The measurement was performed on a test bench using a test cycle that simulates real traffic conditions. Three variants were chosen for burning E85 fuel and the first one was the usage of the E85 fuel without modifications of the engine control unit (variant 1 – E85), the second one was the usage of the E85 fuel with prolonged time of the injection by 28% (variant 2 – E85+) and the last third variant was reference fuel petrol Natural BA95 (variant 3 – N95) for comparison. The results of the measurement have shown that for the variant 1 – E85 there was a significant decrease in the emissions of CO and HC while increasing emissions of $NO_X$ especially at high load. For the variant 2 – E85+ there was a significant increase of the emissions of CO and HC, again especially at high load. Emissions of $NO_X$ have shown a decrease for this variant. $CO_2$ emissions were approximately on the same level for both variants (E85, E85+) in comparison with the variant 3 – N95.

**Keywords:** ethanol, E85 fuel, emissions production.

## INTRODUCTION

The increase in the usage of bioethanol as a fuel in Europe is significant (up to 15% annually) (Beran, 2011). The reason could be the European Parliament and the European Council, which adopted the so called action plan concerning with the issue of biofuels in transport. In the action plan the strategy for achieving the planed 20% substitution of conventional liquid motor fuels with alternative fuels by 2020 is defined (Šebor et al., 2006). Furthermore, according to the European Directive 2009/28/EC on the promotion of the use of energy from renewable sources and amending and subsequently repealing directives 2001/77/EC and 2003/30/EC the target is a 20% share of energy from renewable sources and a 10% share of energy from renewable sources in transport (EU Directive 2009/28/EC; Beran, 2011;). The second reason could be the dependence of Europe on the imported crude oil products. European OECD countries were dependant on the imported crude oil in the year 2007 from about 65% and by 2030 the dependence could increase up to 83%. The transport in Europe is dependant on the crude oil products from about 98% (Šebor et al., 2006; IEA, 2009; Gnansounou, 2010). France is the major consumer of bioethanol in Europe with a 5.41% share of bioethanol on the market (in Sweden it is 5.14%) (Gnansounou, 2010).

The most used fuel with higher share of bioethanol is the E85 fuel, which is made from 85% bioethanol and from 15% petrol. In comparison with the petrol the E85 fuel

has lower energy content and higher density, it also has higher share of oxygen and therefore lower stoichiometric ratio. Furthermore it has lower Reid vapour pressure, higher octane number and therefore an option of using higher compression ratio than petrol Natural 95 and higher heat of evaporation (Pumphrey et al., 2000; da Silva et al., 2005; Laurin, 2006a; Laurin, 2006b; Šebor et al., 2006; Mužíková et al., 2010; Hromádko et al., 2011; Küüt et al., 2011). Taking into account new technologies for its production (second and third generation bioethanol) it could be a perspective alternative fuel which reduces the content of released greenhouse gases and the dependence on the crude oil (Wendhausen et al., 2001; Varga et al., 2003; Sánchez & Cardona, 2008; Goh & Lee, 2010; Hromádko et al., 2010; Eisenhuber et al., 2013; Tutt et al., 2013).

It's well known, that using biofuels such as E85 reduces production of the current most watched greenhouse gas the carbon dioxide. If we neglect $CO_2$ emitted during processing of primary raw materials, bioethanol is actually $CO_2$ neutral (Hromádko et al., 2009; Hromádko et al., 2011; Winthera et al., 2012). This article also describes how this fuel affects other harmful emissions such as carbon monoxide, oxides of nitrogen and unburned hydrocarbons. According to the other experiments in this field (Graham et al., 2008; Graham et al., 2009; Vojtíšek-Lom & Mazač, 2011; de Meloa, 2012) we can expect that emissions of CO and HC will be lower compared to petrol, emissions of $NO_X$ could be higher and emissions of $CO_2$ could be approximately on the same level.

As it was already mentioned, the purpose of the experiment was to measure emissions of $CO_2$, CO, $NO_X$ and HC, produced by light duty petrol vehicle, operated on E85 fuel without engine modifications of the engine control unit and with prolonged time of the injection in simulated real traffic conditions and to compare with operation on petrol Natural 95.

## MATERIALS AND METHODS

The whole experiment was performed on the test bench of the Department of Vehicles and Ground Transport at the CULS Prague.

For the experiment an electric-swirl dynamometer V125 with construction IP23/ICW37 was used. The reaction from the dynamometer was captured via a tensometric sensor with nominal load 2kN and merged mistake 0.5% of the nominal load.

The measurements were performed on the engine Škoda Fabia 1.2 HTP. This engine is a three-cylinder atmospheric in-line four stroke engine, it has overhead cams with 2 valves per cylinder. Max. power is 40 kW at 4,750 rpm, max. torque is 106 Nm at 3,000 rpm and compression ratio is 10.3:1.

The emissions were measured by an emission analyser VMK. This analyser was made by the VMK s.r.o. according to the needs of the Department of Vehicles and Ground Transport at the CULS Prague. The parameters of the analyser are listed in Table 1.

This analyser is using the Non Dispersive InfraRed method (NDIR). This method utilizes the fact, that every gas, which has at least two atoms in its molecule, has unique dependence of the absorption coefficient on the wavelength of the radiation.

As it was already mentioned, the experiment was performed for E85 fuel without modifications of the engine control unit (variant 1 – E85), E85 with prolonging of the time of the injection (variant 2 – E85+) and Natural BA95 (variant 3 – N95). For prolonging of the time of the injection for the second mentioned variant additional control unit plugged between ECU and injectors was used. That means that the input for this unit are the impulses for the injectors sent by ECU and the additional unit is extending them by preset period in percentage and is sending them to injectors. In the case of the variant 2 – E85+, the prolonging of the time of the injection was by 28%.

**Table 1.** Parameters of the emission analyser

| Measured component | Scope | Resolution | Accuracy |
|---|---|---|---|
| CO | 0–10% vol. | 0.001% vol. | 0–0.67%: 0.02% <br> 0.67–10%: 3% from measured value |
| $CO_2$ | 0–16% vol. | 0.1% vol. | 0–10%: 0.3% <br> 10–16%: 3% from measured value |
| HC | 0–20,000 ppm | 1 ppm | 10 ppm or 5% from measured value |
| $NO_X$ | 0–5,000 ppm | 1 ppm | 0–1000 ppm: 25 ppm <br> 1,000–4,000 ppm: 4% from measured value |
| $O_2$ | 0–22% vol. | 0.1% vol. | 0–3%: 0.1% <br> 3–21%: 3% from measured value |

For communication with ECU the diagnostics system VAG-COM was used. This system was primary used for reading values from ECU, such as rotations, load of the engine (in percentage) and the air-fuel equivalence ratio.
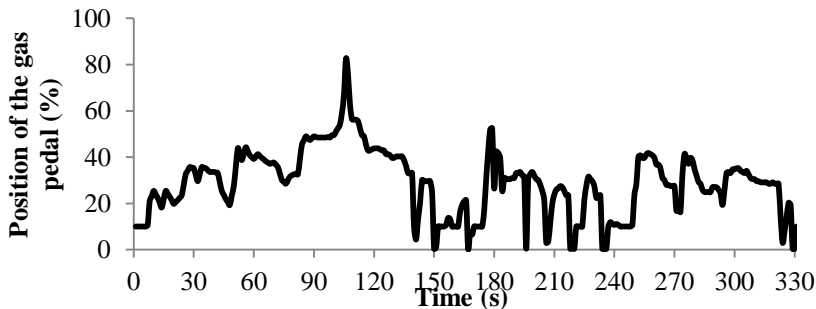


**Figure 1.** Progression of the position of the gas pedal during the test cycle.

The test cycle was acquired, as mentioned above, from real traffic by recording values from the OBD diagnostics system of the vehicle and the length of the cycle is 330 sec (Fig. 1). The whole cycle is characterized by the dependence of the position of the gas pedal on the time of the driving cycle. During the cycle the values of the torque and rotations of the engine are not the same for all variants as a result of the different performance parameters for the used variants (Table 2).

All measured parameters are logged with frequency of 1 Hz into a DBF file on the hard drive of the computer. These measured data were further processed using MS Excel.

**Table 2.** Performance parameters

| Variant | Torque | | Power | |
|---|---|---|---|---|
| | (Nm) | (%) | (kW) | (%) |
| E85 | 107 | 92.2 | 40,7 | 89.3 |
| E85+ | 111 | 95.7 | 41,2 | 90.4 |
| N95 | 116 | 100 | 45,6 | 100 |

## RESULTS

In Fig. 2 the progression of the concentration of carbon dioxide emissions during the driving test cycle is shown. As can be seen, the concentration of $CO_2$ is for all variants approximately on the same level for most of the time of the cycle. The biggest difference is achieved between 90. and 120. sec. of the cycle, where the concentration is decreasing. For variant 3 (N95) and variant 2 (E85+) that decrease of concentration could be caused by worse combustion as a result of the rich mixture at high engine load. This can be also seen in the progression of CO concentration in Fig. 3 and the progression of the air-fuel equivalence ratio in Fig. 4. For variant 1 (E85) is the progression of $CO_2$ between 90. and 120. sec. probably caused by poor mixture, as can be seen in Fig. 4. Decreases in the concentration of $CO_2$ which can be seen for all three variants between 150. and 240. sec. of the cycle are connected with shortening of the time of the injection due to the sudden reduction of the fuel supply (Fig. 1) and thereby with sudden reduction of the engine load. This also shows the value of the air-fuel equivalence ratio in Fig. 4, which significantly increases in these places.
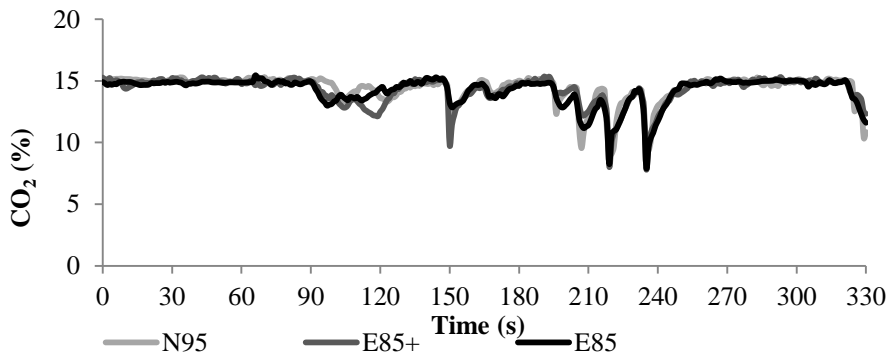


**Figure 2.** Progression of $CO_2$ during the test cycle.

From Fig. 3 it is evident that the concentration of CO was significantly higher for variant 2 (E85+) than for variant 3 (N95), this is caused by the fact that between 90. and 120. sec. of the cycle for variant 2 a richer mixture was burned than for variant 3 (Fig. 4). For variant 1 (E85) a significant decrease in concentration of CO compared to variant 3 (N95) can be seen. That is most probably caused by better combustion efficiency as a result of a poor mixture.

318
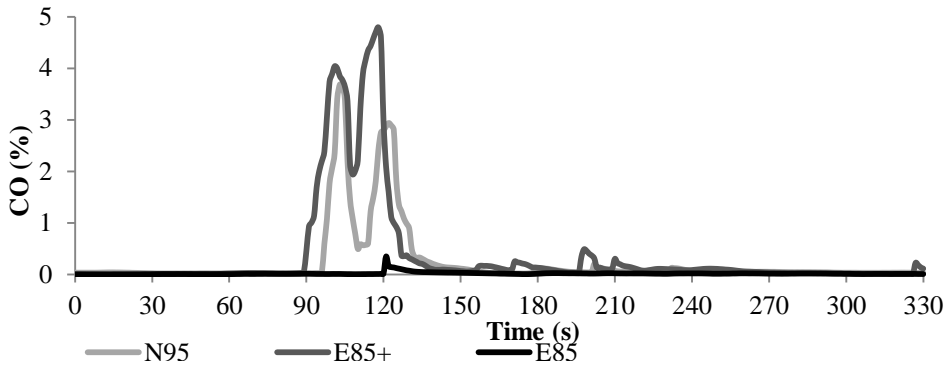
**Figure 3.** Progression of CO during the test cycle.
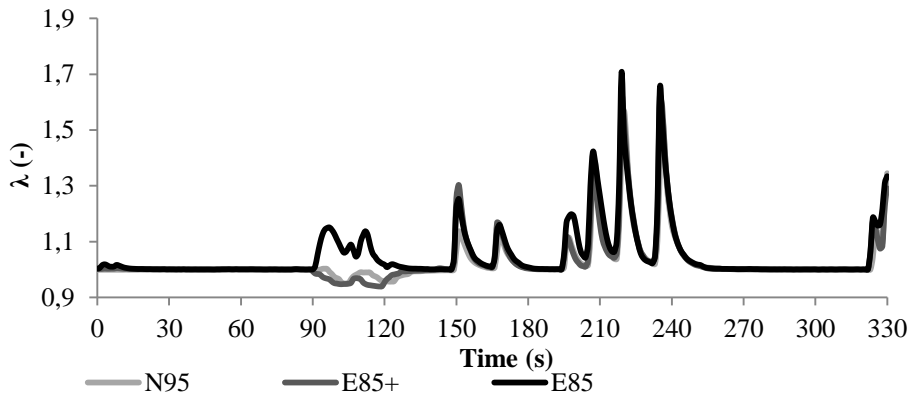


**Figure 4.** Progression of λ during the test cycle.

In Fig. 5 the progression of the concentration of $NO_X$ during the test cycle is shown. As can be seen for variant 1 (E85) the concentration is order of magnitude higher than for variant 3 (N95). That is probably caused by higher temperature as a result of combusting of the poor mixture. Another reason may be poor three–way catalyst efficiency for oxides of nitrogen as a result of lack of CO and unburned hydrocarbons to oxidation. For variant 2 (E85+) it can be seen that the concentration of $NO_X$ between 90. and 120. sec. of the cycle is lower than for variant 3 (N95). That can be explained by combusting of richer mixture that creates higher concentration of CO, which ensures good efficiency to the three-way catalyst for oxides of nitrogen.

The progression of HC emissions is shown in Fig. 6. The biggest difference between variants 2 and 3 is again in the places with the highest engine load. As a product of prematurely stopped oxidation reactions, HC are usually located in the exhaust gases along with CO, which can be seen in variant 2 (E85+) in Fig. 3. On the contrary, for variant 1 (E85), where almost no CO was, lower concentration of HC can be also seen.
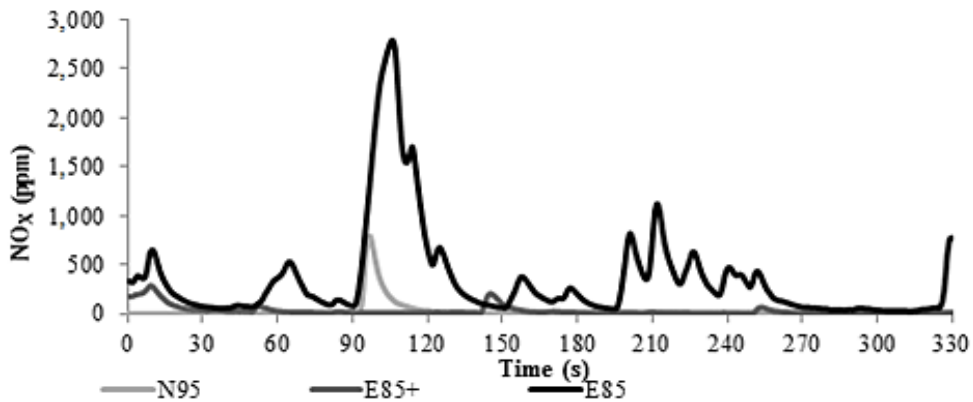
**Figure 5.** Progression of $NO_X$ during the test cycle.

Even after repeated measurements using driving cycle for variant 1 (E85) without conversion, the ECU was reporting an error message indicating too poor mixture. Therefore the engine is not able to fully adapt to operation on E85 fuel without customization of fuel amount supply.
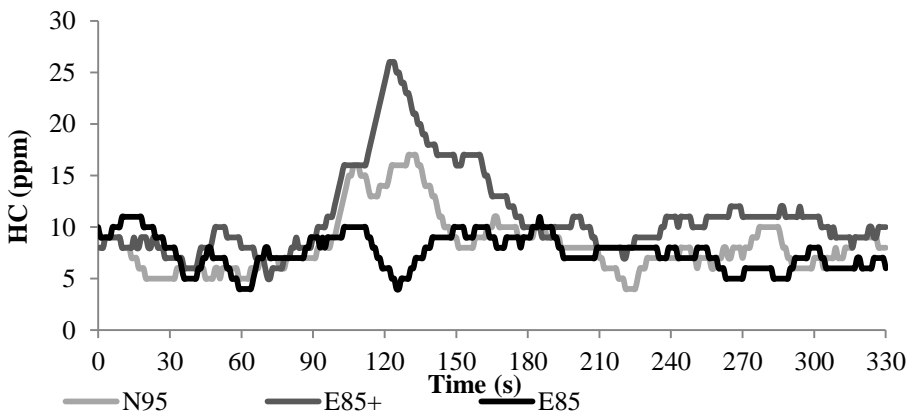


**Figure 6.** Progression of HC during the test cycle.

## CONCLUSION

In Table 3 the mass expression of the emissions, produced during the cycle is listed. These values were counted from knowledge of the mass flow of the fuel, immediate value of the air-fuel equivalence ratio, stoichiometric ratio and concentrations of the individual components of the emissions. For variant 2 (E85+) significant increase of the emissions of CO, almost by 100%, and emissions of HC by 25% compared to variant 3 (N95) occurred. Here the expectations, resulting from the literature research, listed in the introduction, were not verified. The reason is most probably too big prolonging of the time of the injection, which was 28%. In the contrary, emissions of $NO_X$ decreased most likely because of good efficiency of the catalyst as a result of increased concentration of CO emissions in the exhaust gases. Furthermore for variant 1 (E85) a significant decrease of the emissions of CO, almost

to zero, and emissions of HC by 25% compared to variant 3 (N95) are indicated. Emissions of $NO_X$ were increased almost eight times. This variant is verifying the expectations because the decrease of CO, HC and the increase of $NO_X$ can be seen.

**Table 3.** Mass expression of individual components of the emissions

| Variant | CO | | $CO_2$ | | $NO_X$ | | HC | |
|---|---|---|---|---|---|---|---|---|
| | (g) | (%) | (g) | (%) | (mg) | (%) | (mg) | (%) |
| N95 | 21.01 | 100 | 879.93 | 100 | 270.2 | 100 | 51.5 | 100 |
| E85+ | 41.33 | 196.7 | 800.06 | 90.9 | 144.6 | 53.5 | 64.4 | 125 |
| E85 | 0.98 | 4.7 | 754.8 | 85.8 | 2,394.3 | 886.1 | 39.3 | 73.3 |

As can be seen in Table 2, according to the expectations the performance parameters of the engine Škoda Fabia 1.2 HTP were reduced as a result of the lower energy content of the E85 fuel. For variant 1 – E85 was the decrement by 10% and for variant 2 – E85+ it was by about 5–10%.

Although the E85 fuel may seem as a suitable bio-substitution for the fossil fuel BA95, the operation of this fuel is problematic especially concerning most of the current sealing elements, which are damaged by influence of the E85 fuel. Also there is a problem with worse starting qualities of the engine during the lower temperatures as a result of the lower RVP. Non-problematic use of this fuel is then possible only for vehicles where the manufacturer explicitly allows using the fuel E85.

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# Possibilities of using vegetable oil to power diesel engines as well as their impact on engine oil

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**Abstract.** The environmental advantages of biofuels cannot only evaluate the final production of pollutants resulting from the combustion of biofuels in the vehicle, but it is necessary to take into account the entire life cycle of fuels including the initial phase of production of raw materials through production to finally the fuel burning vehicle and how it affects the vehicle mechanisms. The Article describes the possibilities of powering diesel engines based on vegetable oils (RME, rapeseed oil) as an alternative to standard diesel fuel. It deals with the properties of biofuels and their potential use in the internal combustion engines by the structural adjustment of the fuel system or the combustion chamber. It also highlights the potential negative impacts of vegetable oils on the machine's operability and the possibility of reducing the negative effects. The article is based on laboratory analysis of tribotechnical diagnostics. They describe the current state of oil, its primary and secondary pollution and wear of the machine. The important method is ferrography to which the main emphasis is focused. The experimental section analyzes the impact of biofuels on the quality of oil used to fill diesel engines, and establishes an optimal oil change interval. For minimization the negative effects of biofuels is tribotechnical diagnosis necessary part of fuels quality evaluation.

**Key words:** rapeseed oil, RME, engine lubrication oil, construction change, tribotechnical diagnostic.

## INTRODUCTION

The phenomenon of the 20th century, the automobile and oil, no other individual sectors of human activity to a degree not affect all our lives. The development of motorization had a major influence on the development and fuel consumption. During the last two decades, along with the impending exhaustion of fuel sources, greatly accelerated the development of automotive technology, particularly in relation to environmental requirements it is necessary to look for new energy sources environmentally friendly. In general, the consumption of energy is an exponential curve, while energy sources, especially fossil, rapidly diminishing, which largely relates to oil. It should also be borne in mind that the oil is not only fuel, but also an important raw material in the chemical industry. The situation in the sources is complicated because two-thirds of oil resources are concentrated in countries in the

Gulf region, which significantly affect world oil production (Hromádko et al., 2009; Hönig et al., 2009).

Currently, spending large sums on the search for alternative fuels for internal combustion engines. In order to alternative fuel to push must be resolved question of performance, range, durability and last but not least cost. Therefore, not biofuels seems like the easiest option in terms of production, engine characteristics, availability as well as the related financial difficulty (Šmidrkal et al., 2008). The main focus in this article is devoted to biofuel most promising for farmers rapeseed oil and its methyl ester (RME). It should be noted that the 'better and more modern vehicle, the more stringent the requirements on fuel quality'. Changes in the design and operation of modern engines prepared complex conditions for the various engine components. Vegetable oils can be used in two ways as a fuel for internal combustion engines. The first is connected minimizing fuel problems and it is a chemical transformation, the second is direct without the use of chemical treatments.

The use of purified rapeseed oil is primarily reduce dependence on petroleum fuel prices, reducing dependence on fossil fuels and means as well as the rise of lucrative farming. However, it is necessary to respect the diversity of parameters of fuel compared to diesel. Tables 1 and 2 provide a comparison of the individual fuel parameters.

**Table 1.** Dominant Parameters

| Parameter | | Diesel | RME | Rapeseed oil |
|---|---|---|---|---|
| Kinematic viscosity (mm$^{-2}$ s$^{-1}$) | -25°C | 5–30 | | 300 |
| | 0°C | 3–14 | 10 | 180–220 |
| | 20°C | 2–8 | 6.3–8,1 | 65–100 |
| | 100°C | 0.7–2 | 1,7 | 6–8 |
| Calorific value – weight (MJ kg$^{-1}$) | | 42.5 | 37.1–40.7 | 37.4 |
| Calorific value – volume (MJ l$^{-1}$) | | 35.2 | 32.7 | 34.4 |
| Heat of combustion (MJ kg$^{-1}$) | | 45.3 | 39.1–42.9 | 39.6 |
| Cetane number | | 45 | 54–55 | 35–50 |
| Density (kg dm$^{-3}$) | | 0.8–0.86 | 0.87–0.88 | 0.91–0.94 |
| Flash point (°C) | | min. 55 | 130 | 300–330 |
| Freezing point (°C) | | -12–0 | -7 | -18–0 |
| Molecular weight | | 200 | 850–900 | 300 |

**Table 2.** Other Fuel Parameters

| | Diesel | RME | Rapeseed oil |
|---|---|---|---|
| Difference in consumption compared to diesel | 0 | +10% | +/-2% |
| Quality of emissions (+/0/-) compared to diesel | 0 | + | + |
| Chemicals in the production | - | methanol, KaOH, NaOH | - |
| Aggression against components | - | aggressive | - |
| Threats to water resources | threat level 2 | threat level 1 | Only in high quantities |

Comparison of the basic physical properties of rapeseed oil with diesel fuel, as specified in the Tables 1 a 2 reveals significant differences between these fuels. Calorific value of fuel decreases with the amount of added RME. The other parameters such as viscosity and flash point indicate, that the direct use of rapeseed oil in a normal diesel engine is not smooth.

The main advantages of using vegetable oils can be summarized as follows:
1) rapid degradation in the soil (within about 3 weeks);
2) renewable source of fuel in the European context;
3) positive energy balance;
4) increase lucrative agricultural activities and by-product formation;
5) reduction of harmful emissions;
6) absence of carcinogenic substances;
7) handling safety (Qi et al, 2013).

The disadvantage of vegetable oils that have a high viscosity. The viscosity can be reduced by heating the oil and appropriately adjusting flow rates of the injection nozzles (Pexa et al., 2013) The fundamental problem stems from the formation of relatively large droplets of oil and its low evaporation, resulting in the formation of carbon. The mean diameter of the droplets in the fuel injection is in a vegetable oil (even when heated to 90°C) by about 80% greater than diesel. This is also the surface tension, so it is necessary to use additives that can be reduced.
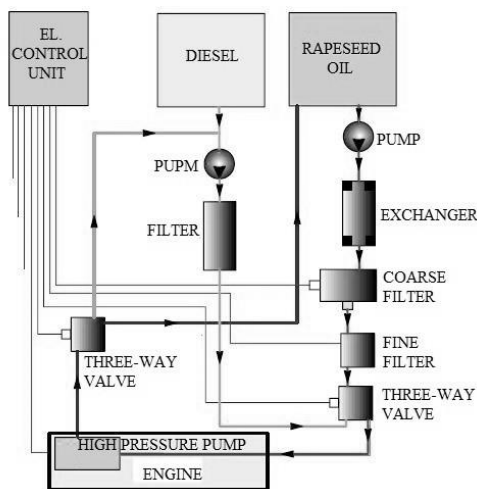


**Figure 1.** Drawing of Dual Fuel System.

In nowadays there are many companies that offer the possibility of conversion to vegetable oil. It is a dual fuel system with two tanks with a modified low-pressure branch (see Fig. 1). At the start of the oil is heated by an electrical heater, after reaching sufficient operating temperature, the driver can choose to switch the operation of the engine on rapeseed oil, which is preheated by heat exchanger (cooling liquid – vegetable oil). If the temperature is at least 60°C, the electronic unit switches and three-way valves in the high pressure pump is fed through the heat exchanger and at

least two filters (coarse and fine) oil. The second three-way valve connects the overflow from the pump to the respective reservoirs. If the driver wants to end the ride must be at least a minute before stopping the engine switch to diesel operation to restart did not go to the oil, because if there 's cooled down, it is not pumped due to high viscosity. If they do, should not allow the control unit to stop the engine running, or at least should be the driver is alerted by an acoustic signal.

Also one possible solution is with one of the fuel tank based on an electrical preheating vegetable oil before the start and during engine operation. This system requires the use of other injectors. To overcome the higher pour point, depending on the outside temperature added to the tank minimal amount of diesel.

## MATERIALS AND METHODS

Experimental analysis of the impact of biofuels on diesel oil charge is based on laboratory evaluation samples by tribotechnical diagnostics.

Tribotechnical diagnostic techniques applied to conditions follows three interconnected and inseparable objectives:

1. Determining the life of lubricant on the basis of the degree of wear and tear or depreciation of lubricant (oil) contamination secondly primary (arising from thermo-oxidative processes in the actual lubricant) as well as secondary dirt, getting to the operating lubricant from the outside (e.g. abrasion machine parts or in the form of intake silica dust).

2. The monitoring wear of moving and stationary parts. It is also important observations trend wear as monitoring increases wear metals (Fe, Al, Cr, Pb, Sn, etc.), which corresponds to the monitoring of secondary contamination.

3. Determining the optimal lubricant change interval (operating oil) is directly dependent on two previous findings mentioned in 1. and 2. Oil change interval is determined with respect to engine load, the working conditions and the condition of the engine.

The experiment is based on the assumption that it is impossible to seal the combustion chamber so as not to dilute the oil fill unburnt fuel. In the case of the impact of biofuels on oil filling is still a neglected issue, which however has a significant effect in terms of evaluating the use of non-standard fuels (Aleš, 2009).

The conditions for the realization of this experiment was the selection of a group of identical or similar cars (engines) operating under similar operating conditions. It is necessary to take into account cold starts, the proportion of short and long routes and the effect of STOP & GO motor mode typical of urban traffic.

Measured oil sample comes from three test vehicles Renault Mégane 1.5 dCi with a similar operation. The first vehicle that uses their power to FAME (B100), the latter with built-in dual-fuel system burning **rapeseed oil** + **diesel** and for comparison were analyzed oil samples from vehicles powered by conventional **diesel** fuel. In the experiment were successively sampled during motor oil change intervals of every three of the vehicles on which they were made these tribotechnical tests:

1. Determination of total impurities (% CN) using the apparatus TCM- U, whose principle is to evaluate the light transmittance of the oil filled in the microcuvette.

2. Determination of kinematic viscosity by Ford spout cup with a Ubbelohde viscometer hanging level. The test is based on the standard measurement of the time required to flow a certain amount of oil specified capillary at a given temperature. The results can be seen on Fig. 2.

3. Determination of flash point in open crucible by Cleveland. This is important not only for safety regulations (risk of fire), but also indicates contamination with fuel. The results can be seen on Fig. 3.

4. Particle analysis exploited oils with a final determination of the mode of wear and surface wear (WPC) on the unit PMA – 90 ferrographical method.

Ferrography is a technique that allows the size sorting, separating the particles of the metal nature (especially ferromagnetic) from operating lubricants and other accompanying substances generated primary pollution, such as carbon fiber and a number of so-called soft dirt when washing ferrographical tracks washed away (Ales et al., 2013).

The acquisition of ferrogram will then only assorted metal wear so that at the beginning of the track are particles with the largest volume (the largest magnetic susceptibility) and at the end of a track captures the volume smaller particles. This allows the divergent magnetic field of ferrograph.

1. Each friction pair, each node produces frictional wear particles of specific sizes and shapes, characteristic of the mode wear a pair of the materials.

2. With the increasing intensity of wear (or wear at elevated mode) grows and the shape and size of wear particles, but also by changing the ratio between the large and small particle abrasion.

3. When the machine wear monitors both the overall level of wear (WPC) the indication spectrographic analysis and, secondly, the intensity of wear.

Using PMA – 90 analyzer (capillary analyzer magnetic particles in fluids) is collected input data to compute the level of wear (WPC). The principle consists in the deposition of metal wear particles (especially ferrographic) in thin-walled glass capillary action of a divergent magnetic field. The particles are deposited in the capillary at certain distances depending on their magnetic susceptibility . Save particles in the capillary volume is done. Recorded fotodensity (infrared diode sends a beam through the capillary to the detector) is evaluated in an electronic device.

Used oil was refiled in engine each 15,000 km. Oil sample was taken after each 3,000 km. Samples were numbered according oil refilling and sampling procedure by to digits code. The analyzed oil samples were taken from vehicles to each of the replacement interval was measured successively five samples for three drain intervals. As an example, the pattern of change parameters of oil filling samples taken from the Renault Mégane 1.5 dCi with integrated bi-fuel system for a diesel drive + purified rapeseed oil.

## RESULTS

The measured results of oil samples are plotted on nomogram wear trend (Fig. 4), the essence of which is the application of discriminant analysis. Discriminant analysis is a specific method for multivariate statistical analysis. Historically, the first

comprehensive set of multivariate statistical methods in theory elaborated in the literature and applied in practice. All measured and calculated values of the level of wear WPC (metal wear particles) are plotted on the x-axis, they are assigned appropriate values determine the total impurities CN % on the y-axi, where it can be read at what stage of wear of engine oil sample analyzed located (Fig. 5).
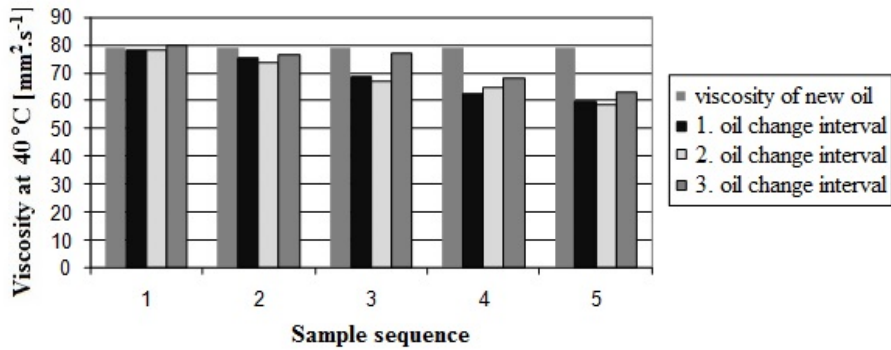


**Figure 2.** Comparison of kinematic viscosity changes with the new oil drain intervals for individual.
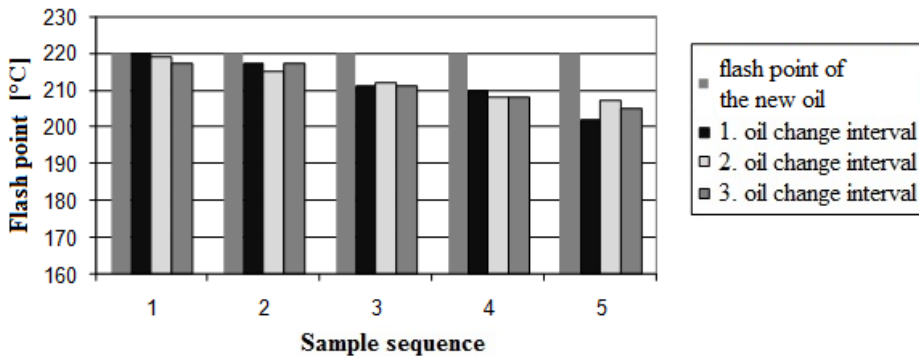


**Figure 3.** Comparison of changes in the flash point with the new oil.

Fig. 4 shows the correlation of wear oil filling individual drives. For example illustrates the progress of wear already mentioned, the Renault Mégane 1.5 dCi with integrated bi-fuel system, oil + rapeseed oil. The figure 4 shows also compared with samples from vehicles Renault Mégane powered by other fuels: diesel and RME.

To construct a nomogram the wear should be carried out to correct the WPC $WPC_K$, taking into account also the amount of new oil added for the full replacement interval.

$$WPC_K = WPC \cdot K_C \quad [\% \cdot ml^{-1}] \tag{1}$$

$$K_C = K_M \cdot K_{NM} \tag{2}$$

and the value of $K_M$, $K_{NM}$ calculated according to equation

$$K_M = \frac{V_k + V_{tu}}{V_k} \qquad (3)$$

$$K_{NM} = \frac{M_{ntu}}{M_{stu}} \qquad (4)$$

where: $V_k$ (l) − the volume of oil in the casing; $V_{tu}$ (l) − the amount of oil added in the whole interval exchange; $M_{ntu}$ (l) − standardized fuel consumption; $M_{stu}$ (l) − actual fuel consumption.
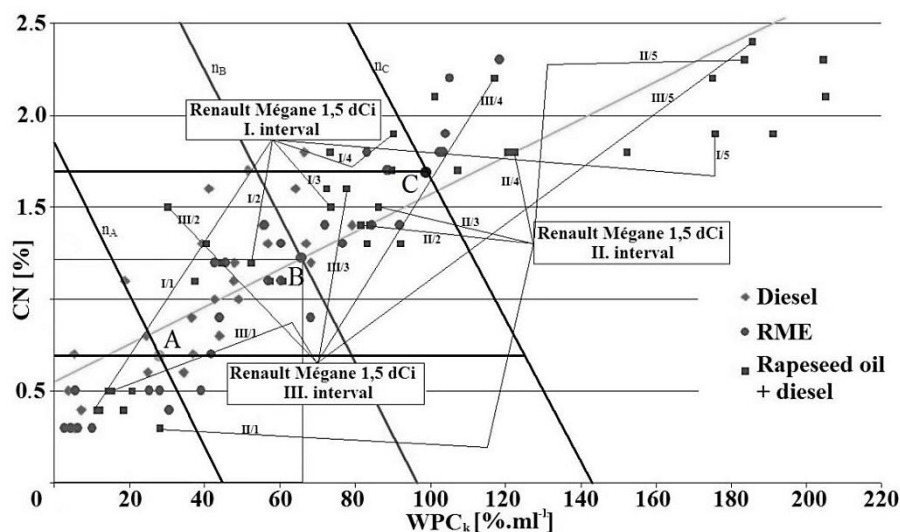


**Figure 4.** Construction of nomogram: $B$ − average of all the values plotted in the graph; $A$ − average of the poorer samples; $C$ − average of the better specimens.

The results were compared with vehicles powered by conventional diesel fuel. In the case of type RME (B100) leads to higher levels of abrasion wear (WPC) and the overall pollution (% CN) exploited oils, although the decrease in viscosity is not as significant as for diesel. Effect of methyl engine oil, however, causes a greater increase of wear particles, faster degradation and the need to shorten the replacement interval oil.

Results of the effect of rapeseed oil to the oil filling systems from bi brings alarming findings. The first concerns again the values of total level of abrasion (WPC), in this case, the drive against the RME exaggerated, even though the system uses two tanks and propulsion diesel fuel. Surprisingly, however, with values up to extremely high compared with the change intervals of vehicles that run only on diesel.

In a surprising may also indicate relatively high values of total pollution (% CN) exploited oils, which reached more than two percent values. When a significant drop in viscosity leads to loss viscosity reserves and higher increase of wear particles.

Reducing the negative effects of biofuels on the one hand in a very careful adherence oil replacement interval from the start of operation of these vehicles, suitable oils, oil or dust filter and adapt to the structural characteristics of the motor vehicle.
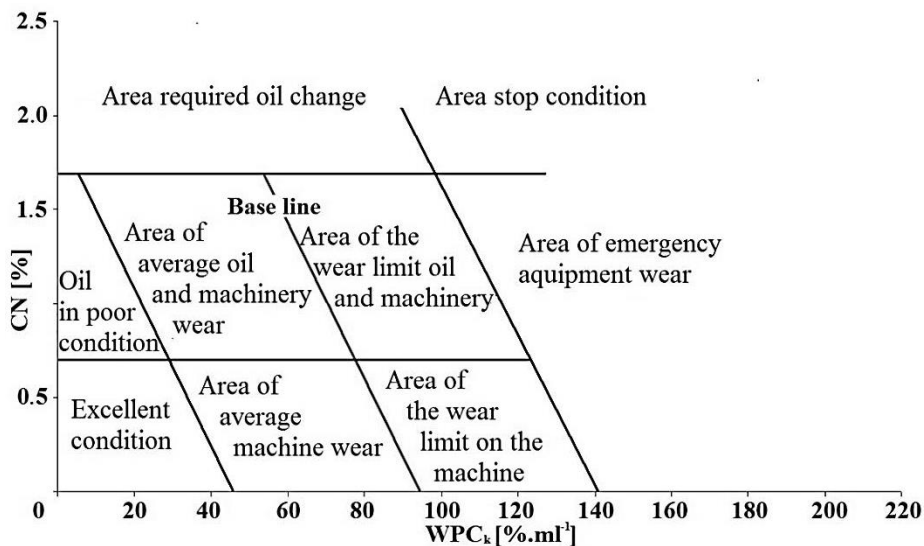


**Figure 5.** Nomogram the wear.

The degradation of the oil filling also affects the type of operation in which the vehicle is predominantly occurs . Vehicles in urban traffic compared to vehicles which prevails intercity traffic, the refill interval shorter, since an increase in urban wear contributes just STOP & GO mode (from the junction to the junction). The wear values (WPC) and total impurities (% CN), which should be given the most attention are also the dominant parameters for determining the replacement interval. Based on the analyzes of the experimental arises recommendations to shorten the interval exchange at rated vehicles in both cases biofuel. Compared with conventional drive diesel cars would drive by on pure RME should lead to exchanges of oil after about 13–15,000 km. As can be seen from Figs 4 and 5, the samples are largely found in the field of accidental wear, in the case of dual-fuel systems, diesel – rapeseed oil by this change intervals therefore not exceed about 9,000 km (considering mixed traffic – urban and interurban).

Preventive replacement of the oil filling may seem uneconomical, but subsequent negative effects have a decisive impact on uptime and the need for subsequent repair or replacement of parts, whether in the case of the oil, so if for example, injection pumps in the selection of inappropriate biofuels (FAME fats of animal recycling, used frying oils, etc.).

# CONCLUSIONS

First, the purified rapeseed oil was in the case of production and use, for instance in the farm to cut fuel costs. From the point of view fuel running diesel engine with its high cetane index (CI around 50 units) finer, fuel is biodegradable, which may allow easier entry of agricultural machinery in times of extreme protected areas or places near water sources and burning produces minimally harmful emissions and substances contained therein are not carcinogenic.

The greatest enemy of smooth usage is motor temperature regime influenced by the nature of the power load. Viscosity rapeseed oil is significantly higher than for diesel fuel, which restricts the use of such dual fuel systems. The cold properties are worse than diesel or RME and fuel has a lower oxidation stability, causing the formation of sludge in storage.

In the case of the use of biofuels, it is necessary to define when and how they will be used. Since this is a non-standard fuel, should not be ignored chemical properties not only with regard to such oxidative stability and carbonization components, as well as characteristics of the vehicle, without which the fuel itself or not justified. As apparent from the above experiment, one can never provide the combustion chamber so as to prevent mixing of the oil filling unburnt fuel. This results in a change in viscosity and increase WPC (metal wear particles), which causes degradation of the oil and wear of the lubricated parts. It is therefore necessary to respond to the diversity of fuel and reduce replacement interval for oil.

With instituted mandatory admixture of bio-components and a gradual increase in the percentage of standard fuels are questions the impact of biofuels on the vehicle one of the most discussed issues of the problem. Despite a number of positive (environmental, economic, etc.), bringing biofuels as well as some negatives. As also evident from the evaluated experiment, so next elections alone fuel must take into account the impact on the oil, which should not be neglected in order to minimize risks and to secure the smooth operation of the vehicle.

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# Use of butanol as a fuel for internal combustion engines

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**Abstract:** Currently, the focus of the research and development is devoted to the wider use of fuels of plant origin focused on the possibility of producing a higher quality and use of motor fuel other than bioethanol. BioButanol is thus not only a promising alternative fuel for gasoline, but also a possible replacement for bioethanol as a fuel for internal combustion engines for transportation. Butanol can be produced virtually with the same ingredients as bioethanol, but in terms of fuel property, it is a preferable alternative to bioethanol. The efficient technology for its production by direct fermentation of simple sugars by fermentation, enzymatic hydrolysis or modified polysaccharides is currently the subject of intensive research work. The paper presents fuel properties of butanol and simultaneously compared with the properties of gasoline and bioethanol. It also specifies the advantages and disadvantages of its use both in mixtures and in its pure form. The article also reviews the experimental analysis of emissions in the driving cycle fuel consumption of butanol. Mixtures of butanol – gasoline 5%, 30%, 50%, 85% and 100% were selected as a fuel without further additions as compared to the automotive gasoline and ethanolic E85. Switching to fuel based butanol in FFVs is not a technical problem, particularly based on the comparison with its demonstrable benefits over bioethanol. The development of renewable sources of carbohydrates from agricultural crops butanol can also help reduce imports of petroleum fuels in support of agriculture, availability of drinking water and an increase employment in the region.

**Key words:** butanol, bioethanol, gasoline, emissions, water.

## INTRODUCTION

Biofuels have become an integral part of everyday life in modern society. Bioethanol and methyl esters of fatty acids are a regular part of producers of gasoline and diesel fuels, although in limited quantities, but intense pressure on replacing fossil fuels with bio-components constantly growing. Despite the considerable problems associated with high production costs, technical and logistical problems and negative impact on food prices in the first case of biofuels generation biofuel development is directed to the second generation, whose resource base is agricultural non-food biomass and waste. Among biofuels second generation is sorted and butanol (Šebor et al., 2006).

BioButanol (n-Butanol, Butan-1-ol) is an alternative to bioEthanol, which is currently commercially produced and used as a component of motor gasoline or as

E85. BioButanol has not only a higher calorific value than bioethanol, is not hygroscopic, but its characteristics even closer to gasoline and can be used as 100% bioButanol fuel (Pospíšil et al., 2014).

Traditional materials for the production of butanol are starchy crops (cereals, maize, potatoes) and molasses from sugar cane or sugar beet. In consideration, however, susceptible to other alternative materials such as whey, waste glycerol or unicellular algae accumulating starch in their cells.

Large positive or negative emotions currently produce the second generation biofuels (especially ethanol but also butanol), in the manufacture of which is the main source of cellulose saccharidic of different materials, e.g. straw or waste paper waste and energy crops. The release cellulose from lingocellulosic matrix and its subsequent cleavage to glucose units either chemically or enzymatically but the raw material compared to conventional sources saccharidic more costly (Patáková et al., 2010)

Selection of raw material depends on the enzymatic equipment of microorganisms. Cultures of Clostridium acetobutylicum and C. beijerinckii are capable of use as a substrate a variety of monosaccharides, disaccharides, and unlike yeasts and polysaccharides (starch). They have the enzymatic equipment for fermentation polysaccharides type of cellulose and hemicellulose . Such materials must first be subjected to hydrolysis to simple sugars by the action of hydrolytic enzymes or dilute acids (Ezeji et al., 2007; Melzoch & Rychtera, 2012).

Raw materials for ABE fermentation are distinguished:
1) starchy (potatoes, corn, wheat, rice);
2) sugary (sugar beet molasses, whey);
3) lignocellulosic (straw, wood).

Since in the original raw sugar and starchy raw material accounted for about 60% of the cost of producing butanol, looking for the cheap raw materials such as lignocellulosic materials and waste products of industrial production rich in carbohydrates, which would significantly reduce costs. Unlike yeast, clostridia are capable of producing solvent ferment greater variety of carbohydrates. Of the monosaccharides are hexoses (glucose, galactose), but also pentoses (xylose, arabinose, ribose ), disaccharides (sucrose, mannose) and polysaccharides (starch). (Groow et al., 1992; Campos et al., 2002). In Table 1 are shown the dominant parameters ethanol and butanol in comparison with gasoline parameters. Table 2 shows dependence of the calorific value of gasoline on the content of ethanol and butanol.

In the evaluation of usable fuel in terms of energy content are distinguished and specific terms of energy consumption. The usable heat energy contained in the fuel is expressed either by referring to a unit mass of the fuel heating value is called the weight of the unit kJ kg^{-1}, or less frequently by referring to the unit volume of fuel, then it is a volumetric calorific value, reported in units of kJ kg^{-1}. (Hromádko et al., 2011). The total thermal energy of the fuel is expressed as heat of combustion, which can be described as all the energy obtained by burning 1 kg of fuel, including cooling the flue gas to the original temperature. The gases are of course in automotive engines emitted into the air so that condensation energy contained therein is not used. Utilised amount of energy is then expressed as calorific value, which is always less than the heat of combustion. (Mužíková et al., 2010). Gasoline with a density of 762 kg m^{-3} has

a calorific value of approximately 42.6 MJ kg$^{-1}$. Butanol has a lower calorific value than gasoline, but higher than the 14.5% ethanol.

**Table 1.** Comparison of basic parameters ethanol, n-Butanol and the gasoline fuel

| Parameter | Ethanol | Butanol | Gasoline |
|---|---|---|---|
| Chemical formula | $C_2H_5OH$ | $C_4H_9OH$ | $CH_{1,87}$ |
| Density at 15 °C(kg dm$^{-3}$) | 0.79 | 0.81 | ~ 0.73 |
| Kinematic. viscosity at 20°C (mm$^2$ s$^{-1}$) | 1.52 | 3.64 | 0.4–0.8 |
| Boiling point (°C) | 78 | 118 | 30–215 |
| Calorific value (MJ kg$^{-1}$) | 26.8 | 32.5 | 42.9 |
| Heat of vaporization (MJ kg$^{-1}$) | 0.92 | 0.43 | 0.36 |
| Vapor pressure (kPa) | 19.3 | 18.6 | 60–90 |
| Mixed octane number | | | |
| RON | 106–130 | 94 | 95 |
| MON | 89–103 | 80–81 | 85 |
| Oxygen content (% by weight) | 34.7 | 21.6 | < 2.7 |

The aim of the measurements referred to in article is to evaluate the fuel properties of a mixture of biobutanol with gasoline compared to E85 fuel and gasoline and emission analysis of these mixed fuels and pure gasoline.

**Table 2.** The dependence of the calorific value of gasoline on the content of ethanol and butanol

| The oxygen content in gasoline (% by weight) | The ethanol content in gasoline (% v/v) | Calorific value gasoline with $CH_3OH$ (MJ l$^{-1}$) | The n-Butanol content in gasoline (% v/v) | Calorific value gasoline with $C_4H_9OH$ (MJ l$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 32.9 | 0.0 | 32.9 |
| 0.4 | 1 | 32.8 | 1.6 | 32.8 |
| 1.1 | 3 | 32.5 | 4.8 | 32.6 |
| 1.8 | 5 | 32.3 | 8.0 | 32.4 |
| 3.7 | 10 | 31.7 | 16.0 | 31.9 |
| 2.7 | 7.3 | 32.0 | 11.7 | 32.2 |

## MATERIALS AND METHODS

To evaluate the effect of n-Butanol on gasoline parameters were selected mixed with the working title:

BUT 5: mixture of 5% n-Butanol and 95% gasoline;
BUT 30: mixture of 30% n-Butanol and 70% gasoline;
BUT 50: mixture of 50% n-Butanol and 50% gasoline;
BUT 85: mixture of 85% n-Butanol and 15% gasoline;
BUT 100 100% n-Butanol.

For experiments was used gasoline internal combustion engine Skoda Fabia 1.2 HTP, whose basic parameters are listed in Table 3.

**Table 3.** The parameters of the test engine

| Engine code | AWY (BMD) |
|---|---|
| Construction | 3 cylinder in-line engine<br>2 valves per cylinder |
| Stroke volume | 1,198 ($cm^3$) |
| Cylinder Bore | 76.5 (mm) |
| Stroke | 86.9 (mm) |
| Compression ratio | 10.3 : 1 |
| Max power | 40 (kW) by 4,750 (1 $min^{-1}$) |
| Max torque | 106 (Nm) by 3,000 (1 $min^{-1}$) |
| Engine control unit | Simos 3PD (multipoint injection) |
| Fuel | gasoline 95 |
| Emission standard | EU4 |
| $CO_2$ emissions | 142 (g $km^{-1}$) |

Measurements under laboratory conditions was carried out on a test bench (Fig. 1), which was placed above the internal combustion engine.

In Table 4 are shown the dominant parameters of swirl dynamometr. To evaluate the immediate emissions, an emission analyser VMK was used (Fig. 2). Detailed technical parameters are listed in Table 5. The instrument is designed to measure the concentrations of carbon monoxide (CO), carbon dioxide ($CO_2$), hydrocarbons (HC), nitrogen oxides ($NO_X$) and oxygen ($O_2$) in the exhaust gases of internal combustion engines with internal combustion mixture.
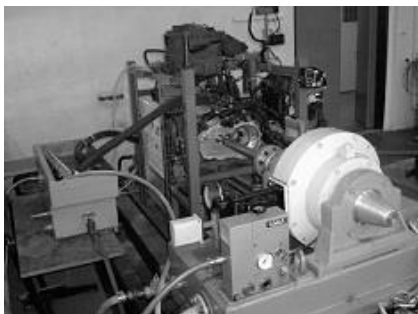


**Figure 1.** Swirl dynamometer.



**Figure 2.** Emission analyzer VMK.

**Table 4.** Parameters of swirl dynamometer

| Dynamometer | | Tensometer | |
|---|---|---|---|
| Type | V125 | Rated load (kN) | 2 |
| Performance | IP23/ICW37 | Combined error (%) | 0.5 |
| Engine speed (1 $min^{-1}$) | 300 – 2,500–8,000 | Reproducibility (%) | 0.05 |
| Torque (Nm) | 134 – 478–149.5 | | |
| Power (kW) | 4.2 – 125–125 | | |
| Water flow (l/s) | 0.9 | | |
| Input voltage (V) | 91 | | |
| Input current (A) | 1.7 | | |
| Water pressure (kPa) | 90 | | |
| Weight (kg) | 550 | | |
| EN | 350,000 | | |

**Table 5.** Parameters of emission analyser

| Measured values | Measurement range | Resolution | Accuracy |
|---|---|---|---|
| CO | 0–10% Vol. | 0.01% Vol. | 0–0,67% : 0,02% absolute |
| | | | 0.67% − 10%: 3% measured values |
| $CO_2$ | 0–16% Vol. | 0.1% Vol. | 0–10% : 0.3% absolute, |
| | | | 10–16% : 3% m. v. |
| HC | 0–20,000 ppm | 1 ppm | 10 ppm or 5% m. v. |
| $NO_X$ | 0–5,000 ppm | 1 ppm | 0–1,000 ppm: 25 ppm |
| | | | 1,000–4,000 ppm: 4% m. v. |
| $O_2$ | 0–22% Vol. | 0.1% Vol. | 0–3%: 0.1% absolute |
| | | | 3–21%: 3% m. v. |

The device has been modified so that it can be used for continuous measurement over a longer period of time to measure road or rail vehicles in operation (or other machines equipped with an internal combustion engine). It was also on the bench used diagnostic VAG-COM, which were scanned using the instantaneous value of the engine control unit. Fuel consumption was assessed by gravimetric method. Due to the complex design of modern internal combustion engines, fuel consumption was evaluated by weighing the whole fuel tank including the accessories. The fuel consumption is then evaluated as a weight loss of fuel in the tank (Fig. 10).

An additional control unit by Czech manufacturer EUROPECON MPI-A4 (Fig. 3) was used for adjusting the engine for biofuels. The unit is handling the adjustment of opening time of injectors so a biofuel's different energy per unit volume is compensated. Other unit's job is to provide improve starting of the cold engine by using additional saturation in dependence on the engine's temperature. It is possible to set the starting dose (for starting the engine) and also the saturation when the engine is cold.



**Figure 3.** Additional control unit for E85.
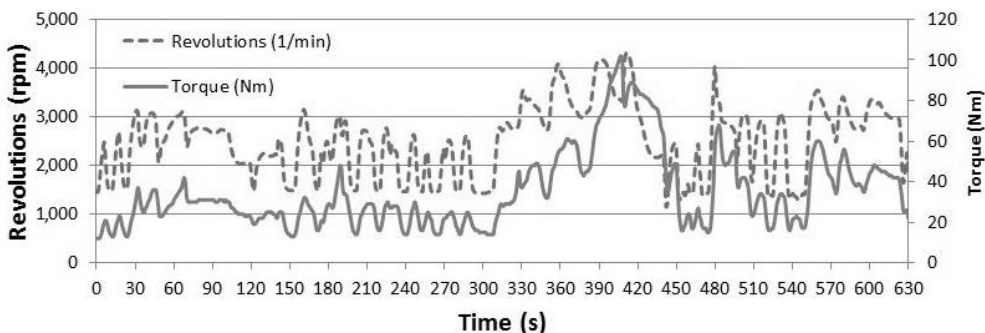


**Figure 4.** Sample of the driving cycle.

# RESULTS

According to current standards for measuring automotive fuels and associated requirements and test methods were performed laboratory analysis of the fuels as a prerequisite for emission analysis. Measured parameters are shown in Table 6.

**Table 6.** Measured parameters of mixture gasoline with n-Butanol

| Parameter | Unit | BUT 5 | BUT 30 | BUT 50 | BUT 85 | BUT 100 |
|---|---|---|---|---|---|---|
| Density by 15°C | kg m$^{-3}$ | 736.16 | 781.5 | 786.01 | 802.95 | 818.1 |
| Beginning of the distillation | °C | 33 | 33 | 35 | 40 | 117 |
| Evaporated by 70°C | % (V/V) | 28 | 20 | 18 | * | * |
| Evaporated by 100°C | % (V/V) | 51 | 44 | 33 | 12 | * |
| Evaporated by 150°C | % (V/V) | 85 | * | * | * | * |
| End distillation | °C | 185 | 117 | 117 | 117 | 117 |
| The distillation residue | % (V/V) | 1.2 | 1.8 | 2.3 | 3.2 | 4.5 |
| Vapor pressure | kPa | 48.0 | 41.5 | 35.5 | 26.0 | 18.5 |
| Index volatility | - | 676.0 | 554.5 | 482.3 | ** | ** |
| Viscosity by 40°C | mm$^2$ s$^{-1}$ | 0.67 | 0.86 | 1.02 | 1.69 | 2.43 |
| Flash-point | °C | ** | ** | ** | ** | 41 |

*value does not exist;
**parameter cannot be evaluated in accordance with the applicable measurement methods for liquid fuels and petroleum products.

The resulting emissions and fuel consumption (Table 7) are based on the driving cycle of the vehicle. Designed driving cycle based on real driving of the vehicle and is adapted to the conditions of the brake post. It is defined by the preset course of the torque and engine revolutions versus time (10.5 minutes). Fig. 4 shows sample of the driving cycle.

**Table 7.** Results emission analysis of the fuels

| Fuel | Emissions | CO | CO$_2$ | NO$_x$ | HC |
|---|---|---|---|---|---|
| B5 | sum. driving cycle (g) | 31.81 | 1,911 | 3.28 | 0.185 |
|  | avg. (g hr$^{-1}$) | 3.03 | 182 | 0.31 | 0.018 |
| B30 | sum. driving cycle (g) | 19.19 | 1,911 | 4.20 | 0.150 |
|  | avg. (g hr$^{-1}$) | 1.83 | 182 | 0.40 | 0.014 |
| B50 | sum. driving cycle (g) | 14.74 | 1,912 | 11.98 | 0.209 |
|  | avg. (g hr$^{-1}$) | 1.40 | 182 | 1.14 | 0.020 |
| B85 | sum. driving cycle (g) | 10.47 | 1,913 | 13.63 | 0.212 |
|  | avg. (g hr$^{-1}$) | 1.00 | 182 | 1.30 | 0.020 |
| B100 | sum. driving cycle (g) | 9.56 | 1,825 | 12.60 | 0.186 |
|  | avg. (g hr$^{-1}$) | 0.91 | 174 | 1.20 | 0.018 |
| E85 | sum. driving cycle (g) | 31.85 | 1,901 | 4.48 | 0.296 |
|  | avg. (g hr$^{-1}$) | 3.03 | 181 | 0.43 | 0.028 |
| Gasoline | sum. driving cycle (g) | 34.83 | 1,924 | 3.48 | 0.208 |
|  | avg. (g hr$^{-1}$) | 3.32 | 183 | 0.33 | 0.020 |

The following Figs 5, 6, 7, 8 and 9 show the sum of values recorded for the entire driving cycle.
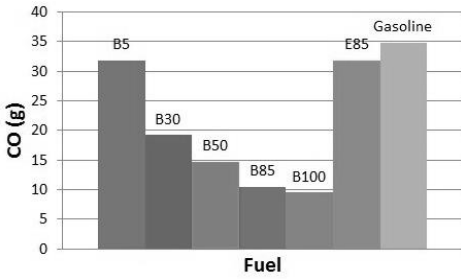
**Figure 5.** CO emissions in the driving cycle (g).
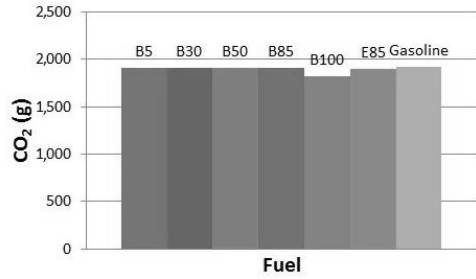


**Figure 6.** $CO_2$ emissions in the driving cycle (g).
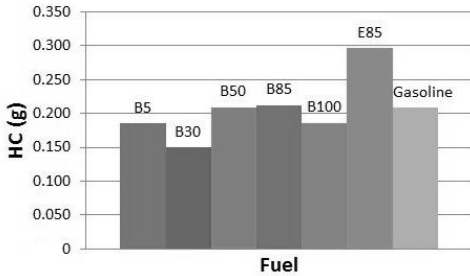


**Figure 7.** HC emissions in the driving cycle (g).
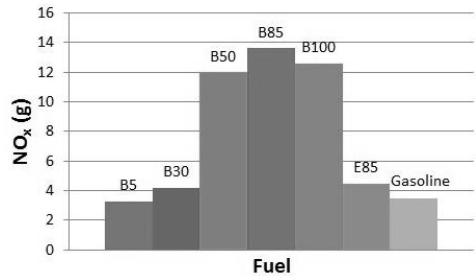


**Figure 8.** $NO_x$ emissions in the driving cycle (g).
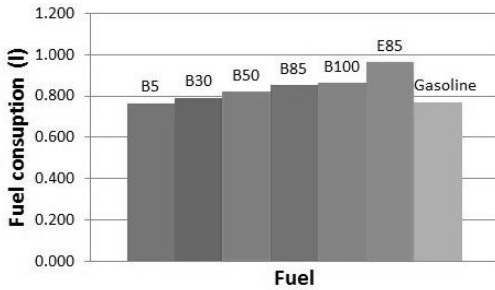


**Figure 9.** Fuel consumption in the driving cycle (l).



**Figure 10.** Position of the tank on the platform scale.

As shown in Fig. 5, with an increasing rate of butanol decreases the production of CO. In the case of production of $CO_2$ can be stated, that there is no fundamental differences between the tested fuels. For the production of $NO_x$ can be seen (Fig. 8), that with increasing proportion butanol increasing $NO_X$ production, which can be attained due to the higher temperature combustion. HC emissions do not show significant differences between the compared fuels production were achieved on the accuracy of the measuring device and the results of the emission component can be taken for reference only. Last Fig. 9 illustrates the results achieved fuel consumption. It is evident, that an increasing share of butanol take to improve fuel consumption. This is primarily due to the calorific value of the fuel used.

## CONCLUSIONS

It can be said that the plant fuel, ethanol and butanol are purposefully added to gasoline. Butanol as an alternative to bioethanol for use of biofuels in transport. Subject to the requirements of EN 228 for the maximum permissible oxygen content in gasoline butanol can be added to the gasoline in volume more than twice the amount of ethanol. Addition of butanol in an amount of 10% (v/v) in gasoline not jeopardize compliance limits according to EN 228, in terms of density, vapor pressure and oxidation stability. Butanol is compared with ethanol better fuel properties – higher heating value, lower vapor pressure, lower heat of vaporization and does not problems with water in the fuel. Both fuels can be produced from the same plant raw material, but the production of butanol is costly. Growing consumer interest in access and butanol stimulate the activity in agriculture and industry. This will affect the growth of production and reduce production costs. Expected future increases in fossil fuel prices and purity requirements combustion and low emissions should be reflected in an increase in the volume of production of butanol. From the viewpoint of fuel properties represents butanol (n-Butanol) preferable alternative to bioethanol and give primarily burn even in its pure form as a 100% biofuel.

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# Influence of the drop size of bioethanol fuel in air-fuel mixture on combustion process of spark ignition engine

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**Abstract:** Bioethanol is widely used as a fuel in spark ignition engines. Brazil and USA are among the largest producers of bioethanol in the world. In order to widen the use of bioethanol as a fuel in spark ignition engines, the combustion process has to be improved. This can be accomplished by dosing bioethanol air-fuel mixture into the engine. Thus, the smaller drop size of the fuel can be achieved than in the air-fuel mixtures formed in regular fuel supply systems. Decreasing the size of the fuel drops decreases evaporation time of the air-fuel mixture and therefore, increases the combustion velocity of the air-fuel mixture. This article gives an overview of using 96.4% bioethanol as a fuel in spark ignition engines when the fuel drop size in the air-fuel mixture directed to cylinder is smaller than in the air-fuel mixture formed in regular fuel supply systems. Results indicate that by decreasing the fuel drop size in the air-fuel mixture, fuel consumption of the engine decreased, while heat-release rate and the combustion velocity of the air-fuel mixture increased.

**Key words:** bioethanol, fuel drop size, spark ignition engine, heat-release rate, combustion pressure.

## INTRODUCTION

Since developing the Otto-cycle engine by N.A. Otto, formation of the air-fuel mixture in the spark ignition engines has considerably improved. In the homogeneous mode, used in Otto-cycle engines, the entire combustion chamber is filled with the air-fuel mixture. In the newest technology, direct injection engines, the fuel is injected directly into the engine's cylinder. Thus, not entire combustion chamber is filled with air-fuel mixture. The advantage of forming a stratified air-fuel mixture close to the spark plug electrode is that it can be ignited even at relative air-fuel ratio $\lambda_{afr} > 1$ thus, decreasing the fuel consumption (Bosch, 2006, Ilves & Olt, 2012). Since the quantity of the fuel directed into the cylinder depends above all on the engine load, the decreased fuel consumption using stratified forming of the air-fuel mixture is achieved only in case of the engine's partial load (Bosch, 2006).

Lately, there has been much discussion about using renewable fuels in the transportation sector. One of the most used alternatives to fossil-based fuels is bioethanol. Brazil and USA are among the largest producers of bioethanol in the world. In different standardised bioethanol fuels (e.g. E85) the absolute alcohol is used.

Production of nonstandard bioethanol with high water content is cheaper compared to the standard bioethanol which makes it a feasible alternative to standard bioethanol. Using bioethanol in direct injection spark ignition engines is complicated

by the viscosity and lubricating properties of bioethanol (Ma et al., 2004). In particular this concerns nonstandard bioethanol. Thus in case of nonstandard bioethanol fuel, it is more reasonable to use indirect fuel supply systems. In order to decrease the fuel consumption of spark ignition engines with an in-direct fuel supply system, the combustion process should be made more efficient. Efficiency of the combustion process in case of homogeneous air-fuel mixture can be increased by decreasing the fuel drop size. The smaller the size of fuel drops in the air-fuel mixture, the faster the air-fuel mixture evaporates in the cylinder and the higher the combustion velocity of the air-fuel mixture (Farouk & Dryer, 2011). This also gives rise to faster heat release rate per crank angle degree (Williams, 1985). Mathematically, the heat release rate is expressed as follows (Heywood, 1988):

$$\frac{dQ_n}{dt} = \frac{\gamma_{hr}}{\gamma_{hr} - 1} \cdot p_c \cdot \frac{dV_c}{dt} + \frac{1}{\gamma_{hr} - 1} \cdot V \cdot \frac{dp_c}{dt}, \tag{1}$$

where: $Q_n$ – is the heat amount that is released as the fuel burns in the cylinder; $t$ – time for rotating the crank; $\gamma_{hr}$ – ratio of specific heats, which in case of ethanol fuel is $\gamma_{hr} = 1.26$ (Kamboj & Kairimi, 2012); $p_c$ – combustion pressure; $V_c$ – cylinder volume.

According to Heywood (1988) the amount of released energy influences the combustion pressure $p_c$, which can be expressed from the fuel mass combustion rate as follows:

$$p_c = \frac{-\dfrac{d(m \cdot u)}{dt} + \dfrac{dQ_{ht}}{dt} + h_{cor} \cdot \dfrac{dm}{dt}}{\dfrac{dV_c}{dt}}, \tag{2}$$

where: $m$ – gas mass in cylinder; $u$ – specific internal energy; $h_{cor}$ – heat-transfer coefficient.

From the previous equation (2), we can express the fuel mass combustion rate $\frac{d(m \cdot u)}{dt}$, heat transfer $\frac{dQ_{ht}}{dt}$ and mass flow rate $\frac{dm}{dt}$ as follows:

Heat transfer $\frac{dQ_{ht}}{dt}$ is expressed as:

$$\frac{dQ_{ht}}{dt} = A \cdot h_{cor} \cdot (T_g - T_{wall}), \tag{3}$$

where: $A$ – combustion chamber surface area; $T_g$ – mean combustion gas temperature; $T_{wall}$ – mean cylinder wall temperature,
while heat-transfer coefficient $h_{cor}$ can be expressed with the combustion rate of the heat flux emitted from the cylinder head as follows:

$$\frac{h_{cor} \cdot d_{cb}}{k} = a \cdot \left(\frac{\rho_{afm} \cdot v_p \cdot d_{cb}}{\mu}\right)^b \rightarrow h_{cor} = \frac{a \cdot k \cdot \left(\frac{d_{cb} \cdot v_p \cdot \rho_{afm}}{\mu}\right)^b}{d_{cb}}, \tag{4}$$

where: $a$ – constant of intensity of charge motion $0.35 \leq a \leq 0.8$; $b$ – constant of intensity of charge motion ($b = 0.7$ with normal combustion); $k$ – thermal conductivity;

$d_{cb}$ – cylinder bore; $\rho_{afm}$ – air-fuel mixture density; $\mu$ – dynamic viscosity; $v_p$ – piston speed.

The equation (2) is expressed from the first law of thermodynamics in case of an open system

$$\frac{dU}{dt} = \frac{dQ_{ht}}{dt} - p_c \cdot \frac{dV_c}{dt} + \sum_i h_c \cdot m_{fr},$$ (5)

where: $\frac{dU}{dt}$ – the maximum internal energy of system materials, and this relation is valid $\frac{dU}{dt} \approx \frac{d(m \cdot u)}{dt}$; $m_{fr}$ – fuel flow rate and in this case $\frac{dm}{dt} = m_{fr}$, which is expressed as follows:

$$m_{fr} = -\frac{m_c \cdot V_{cp}}{V_c^2} \cdot \frac{dV_c}{dt}$$ (6)

where: $V_{cp}$ – combustion chamber volume; $m_c$ – the mass of the air-fuel mixture that is directed to the cylinder in one work cycle, expressed as follows:

$$m_c = V_c \cdot \rho_{afm},$$ (7)

The combustion rate of one fuel drop $\frac{d(m \cdot u)}{dt}$ is expressed according to F.A. Williams (1985):

$$\frac{d(m \cdot u)}{dt} = -4 \cdot \pi \cdot r_{fd}^2 \cdot \rho_f \cdot \frac{dr_{fd}}{dt},$$ (8)

where: $r_{fd}$ – droplet radius in the air-fuel mixture where $r_{df} = \frac{D_{32}}{2}$; $D_{32}$ – Sauter mean diameter.

To evaluate the mass combustion rate of the entire air-fuel mixture, the equation (8) has to be modified to determine the mass combustion rate of the fuel drops found in the entire air-fuel mixture. For this, one fuel drop mass combustion rate $\frac{d(m \cdot u)}{dt}$ has to be multiplied with the total number of fuel drops, $N$, in the air-fuel mixture; and to get the heat emitted per unit of time during combustion, multiply it with the fuel calorific value $Q_{f.teor}$.

$$\frac{d(m \cdot u)}{dt} = -4 \cdot \pi \cdot \left(\frac{D_{32}}{2}\right)^2 \cdot \rho_f \cdot \frac{d\left(\frac{D_{32}}{2}\right)}{dt} \cdot Q_{f.teor} \cdot N,$$ (9)

where: $Q_{f.teor}$ – fuel calorific value; $N$ – total number of fuel drops in the air-fuel mixture, which is expressed as the ratio of the fuel quantity directed into the cylinder $V_f$ and volume of the fuel drops:

$$N = \frac{V_f}{\frac{4}{3} \cdot \pi \cdot \left(\frac{D_{32}}{2}\right)^3},$$ (10)

where $V_f$ – the fuel quantity directed into the cylinder in one work cycle.

Taking into account equations (3), (4), (6), (7), and (9) and replacing them into equation (2), we get the equation for calculating combustion pressure $p_c$; with the help of this, the change of combustion pressure $p_c$ can be evaluated from the diameter of the fuel drops in the air-fuel mixture $D_{32}$. Based on equations (2), (6) and (9), it is a differential equation, which entails two types of derivatives, $\frac{d(\frac{D_{32}}{2})}{dt}$ and $\frac{dV_c}{dt}$. The intensity of fuel drops size change $\frac{d(\frac{D_{32}}{2})}{dt}$ can be deduced from the air-fuel mixture's combustion velocity $v_{afm}$ formula. Therefore, this relation is valid $\frac{d(\frac{D_{32}}{2})}{dt} \approx v_{afm}$, and air-fuel mixture combustion velocity is expressed with the equation (Williams, 1985):

$$v_{afm} = \frac{\lambda}{\rho_{afm} \cdot c_p} \sqrt{4 \cdot \pi \cdot \left(1 + \frac{1}{\lambda_{afr}}\right) \cdot N_k \cdot \frac{D_{32}}{2} \cdot \ln(1 + B)}, \tag{11}$$

where: $\lambda$ – thermal conductivity; $c_p$ – specific heat at constant pressure; $\lambda_{afr}$ – stoichiometric fuel-gas ratio; $N_k$ – number of fuel drops per unit volume; $B$ – combustion constant.

The change of cylinder volume at different crankshaft angles of rotation $\varphi$ can be expressed as a ratio of cylinder volume change and time

$$\frac{dV_c}{dt} = \frac{V_c + \frac{\pi \cdot d_{cb}^2}{4} \cdot \left(l + d_{cr} - (d_{cr} \cdot \cos\varphi + \sqrt{l^2 - d_{cr}^2 \cdot sin^2\varphi})\right)}{t}, \tag{12}$$

where: $d_{cr}$ – crank radius; $l$ – connecting road length;

following from the above, the combustion pressure $p_c$ calculation model is expressed as follows:

$$p_c = \frac{t}{V_c + \frac{\pi \cdot d_{cb}^2}{4} \cdot \left(l + d_{cr} - \left(d_{cr} \cdot \cos\varphi + \sqrt{l^2 - d_{cr}^2 \cdot sin^2\varphi}\right)\right)} \cdot \left[ 4 \cdot \pi \cdot \left(\frac{D_{32}}{2}\right)^2 \cdot \rho_f \cdot \frac{\lambda}{\rho_{afm} \cdot c_p} \cdot \right.$$

$$\sqrt{4 \cdot \pi \cdot \left(1 + \frac{1}{\lambda_{afr}}\right) \cdot N_k \cdot \frac{D_{32}}{2} \cdot \ln(1 + B)} \cdot Q_{f.teor} \cdot N + A \cdot \frac{a \cdot k \cdot \left(\frac{d_{cb} \cdot v_p \cdot \rho_{afm}}{\mu}\right)^b}{d_{cb}} \cdot$$

$$\left(T_g - T_{wall}\right) + h_c \cdot -\frac{(V_c \cdot \rho_{afm}) \cdot V_{cp}}{V_c^2} \cdot \frac{V_c + \frac{\pi \cdot d_{cb}^2}{4} \cdot \left(l + d_{cr} - \left(d_{cr} \cdot \cos\varphi + \sqrt{l^2 - d_{cr}^2 \cdot sin^2\varphi}\right)\right)}{t} \left.\right] \tag{13}$$

This formula enables to calculate combustion pressure at the different working modes of the engine, depending on the fuel drop size in the air-fuel mixture. To illustrate Equation 13, a sample graph has been compiled (Fig. 1), which characterises the change of combustion pressure depending on the fuel drop size. Technical data of a spark ignition engine of a regular passenger car were used in the calculations. The

calculation results have been transferred to percentages, where $p_{c.max} = 100\%$ and $p_{c.min} = 0$. The range of fuel drop sizes has been chosen $D_{32} = 5…500$ µm.
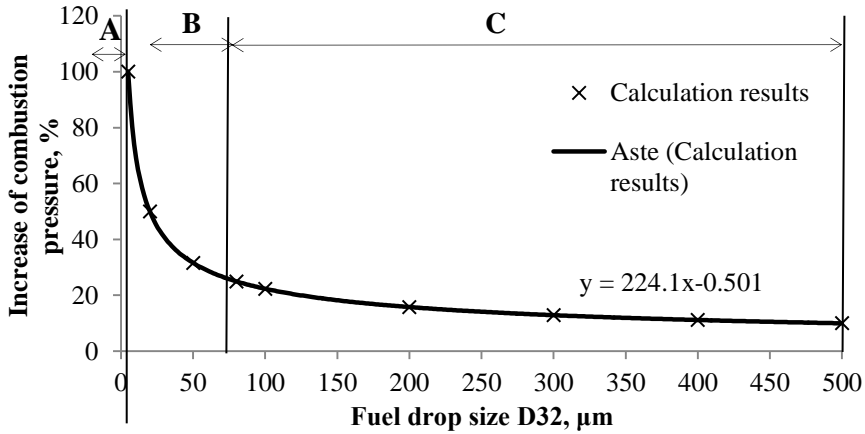


**Figure 1.** Change of combustion pressure depending on fuel drop size in the air-fuel mixture.

Fig. 1 shows that the combustion pressure increases with the decreasing of the fuel drop size. Furthermore, it can be seen that in the region C ($D_{32} = 80...500$ µm) the change in the increase of combustion pressure is considerably smaller with changing drop size, while in the region B (fuel drop size 80 µm to 20 µm) the combustion pressure increases about twice. When decreasing the fuel drop size below 20 µm (region A), combustion pressure increases drastically, which can cause detonating combustion in the engine's cylinder. Thus, it is important to form the air-fuel mixture with the drop size in the region B in order to enable the controlled combustion in the engine's cylinder.

Using the calculation model (Equation 13), increase of combustion pressure in the fuel drop diameter range of 20…80 µm varied with data from different engines 7…60%. An equation of the curve for the calculated characteristic has been indicated on figure 1 as follows:

$$y = 224.1 \cdot x^{-0.501} \rightarrow p_c = 224.1 \cdot D_{32}^{-0.501}, \qquad (14)$$

It enables to evaluate the increase of combustion pressure according to fuel drop size in the air-fuel mixture.

The previous equation (14) characterises combustion pressure $p_c$ change depending on fuel drops' average diameter $D_{32}$. Decreasing fuel drop size increases the combustion pressure $p_c$ in the cylinder, which is caused by increase of the heat release $Q_n$ in unit of time $t$.

This article investigates the spark engine's combustion process when using 96.4% bioethanol as a fuel. More precisely, the bioethanol fuel combustion process is observed using a spark ignition engine with a novel fuel supply system, which guarantees the average fuel drops diameter $D_{32}$ of approximately 23 µm in the air-fuel mixture (Olt et al., 2013). It has to be mentioned that in case of a regular spark ignition engine, the average fuel drop size is $D_{32} \approx 80$ µm in E85 bioethanol fuel injection spray (Gandhi & Meinhart, 2008).

## MATERIALS AND METHODS

For the formation of the small fuel drop size bioethanol air-fuel mixture, a special fuel supply system has been used. More thorough working description of this fuel supply system has been provided in patent document EE 05665 B1 Olt et al. (2013). At least two pulverisers are used in the fuel supply system. The pulverisers have been placed opposite to one another on the same axis therefore, fuel drops in the sprays collide and fragment even further (Olt et al., 2013).

The fuel supply system that enables the formation of air-fuel mixture with small fuel drop size is referred to as a pulveriser fuel supply system. Fig. 2 illustrates the formation of the air-fuel mixture in the pulveriser fuel supply system.

Formation of the air-fuel mixture with small fuel drop size in the pulveriser fuel supply system is ensured by two-step carburation. The first-step carburation occurs in the pulveriser (Figs 2, 11 and 12) and second-step carburation in the intake manifold, where fuel sprays collide with each other (Figs 2, 14) (Olt et al., 2013). The fuel drop size in the air-fuel mixture of the pulveriser fuel supply system has been measured using Malvern Sprytec STP2911. The fuel supply system of Audi ADR 1.8i test engine was used as a reference. The average fuel drop size $D_{32}$ of the fuel spray formed by the regular fuel supply system was determined on the basis of Gandhi & Meinhart (2008).
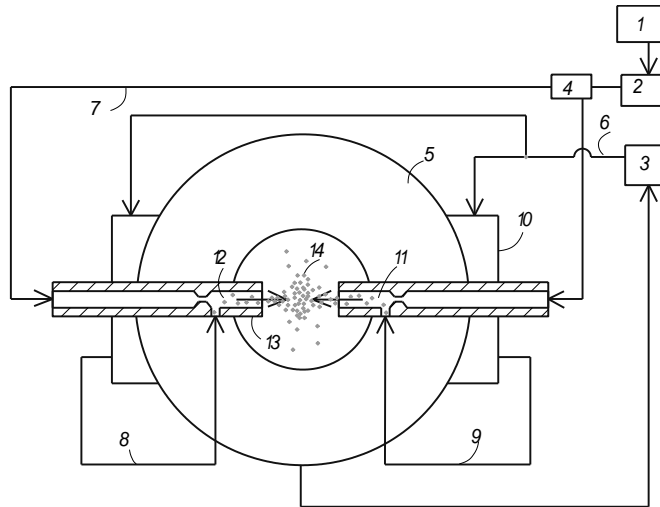


**Figure. 2.** Schematic of the formation of the air-fuel mixture in a pulveriser fuel supply system (Olt et al., 2013). 1 – compressor; 2 – pressure vessel; 3 – fuel tank; 4 – air-pressure regulator; 5 – system corps; 6 – fuel line to fuel-flow regulator; 7 – air line; 8 and 9 – fuel line to pulveriser; 10 – fuel-flow regulator; 11 and 12 – first-step carburation; 13 – pulveriser; 14 – second-step carburation.

In case of a pulveriser fuel supply system, the engine's intake manifold was modified. With the pulveriser fuel supply system the fuel was injected behind the throttle valve, while with the test engine's original fuel supply system the fuel was injected behind the intake valve. Furthermore, the length of the engine's intake manifold decreased. The general tendency is that in case of a long intake manifold, the cylinder's charging efficiency on the crankshaft's rotational speed $n_e = 1,000\ldots5,500$

rpm is better or as good as with a short intake manifold (Heisler, 1995). In order to minimize the effect of the length of the intake manifold on engine output parameters, the engine load during the experiments was chosen $T_e = 30$ Nm and crankshaft's rotational speed $n_e = 3,000\ldots4,500$ rpm.

A modified test bench KI5543 was used during the experiments with the engine load of Te = 30 Nm and crankshaft's rotational speed of ne = 3,950 rpm. As this test bench enables engine break on the bench rotary's rotational speed of $n_d = 1,500\ldots3,000$ rpm (Hutjuk & Tsehov, 1989), gearbox with the transmission ratio of $\eta_{gb2} = 1.84$ was used during the transmission. The test engine's technical data are indicated in Table 1.

**Table 1.** Technical data of the Audi 1.8 ADR engine (Olt et al., 2009)

| Name | Value |
|---|---|
| Fuel supply system | MPI-Bosch Motronic M3.2 |
| Cylinder number | 4 |
| Cylinder bore, mm | 81 |
| Piston stroke, mm | 86.4 |
| Volume, cm$^3$ | 1781 |
| Cooling system | liquid cooled |
| Power, kW | 92 (5,800 rpm) |
| Torque, Nm | 173 (3,960 rpm) |
| Compression ratio | 10.3 |
| Engine stroke | 4 |
| Resisting moment, Nm | 26 |

Combustion pressure in the engine cylinder was measured using AVL 621 and the fuel consumption of the engine using weighing device CAS CI-2001A. The measuring time $t$ of the fuel consumption was 60 s. Based on the combustion pressure, the heat release $Q_n$ and respective heat release rate $\frac{dQ_n}{d\varphi}$ were calculated. Heat release rate was calculated according to Equation 1. Heat release $Q_n$ is expressed as the follows (Heywood, 1988):

$$Q_n = \frac{dQ_n}{d\varphi} + Q_{n.\varphi-1} \tag{15}$$

where: $Q_{n.\phi-1}$ – the net heat per crank angle degree that was released during the combustion process; $\varphi$ – crankshaft angle.

Other parameters characteristic to the engine work have been calculated according to the standard GOST 18509-88.

## RESULTS AND DISCUSSION

The experimental data shown in Table 2 characterise more precisely the fuel drop size in the air-fuel mixture. $D_{10}$ is the arithmetic mean of the droplet diameter, $D_{50}$ is mass median diameter, where 50% drops have smaller and 50 % bigger diameter, $D_{90}$ is the diameter of drops of which 90% are smaller (Malvren, 2012), $D_{32}$ is Sauter mean diameter, and $D_{43}$ is Herdan mean diameter, which characterises the fuel drop size most frequently found in the injected fuel spray (Sescu, 2011; Malvren, 2012). According to Gandhi et al. (2008) Sauter mean diameter is used to characterise the fuel drop size

found in the injection system of a regular spark ignition engine. Therefore, Sauter mean diameter $D_{32}$ was taken as the basis to describe the air-fuel mixture formed in the pulveriser fuel supply system as well. Experiments showed that the average Sauter mean diameter $D_{32}$ in the air-fuel mixture formed by a pulveriser fuel supply system is approximately four times smaller than in the air-fuel mixture formed by the engine's original fuel supply system. The results of engine tests performed with both fuel supply systems are presented in Table 3. The tests were performed at constant engine load and crankshaft's rotational speed. In order determine the impact of the air-fuel mixture on the combustion process, the same ignition angle $\alpha_i$ given by the test engine's original control unit settings was used during testing.

**Table 2.** The characteristics of air-fuel mixture of 96.4% bioethanol fuel formed by a pulveriser fuel supply system, where $D_{10}$ is the arithmetic mean droplet diameter, $D_{50}$ Mass Median Diameter, $D_{90}$ drop size of which 90% of the fuel drops are smaller (Malvren, 2012), $D_{32}$ Sauter mean diameter, and $D_{43}$ Herdan mean diameter (Sescu, 2011; Malvren, 2012)

| Name | Fuel system pressure |
|---|---|
| $D_{10}$ (µm) | 12.22 |
| $D_{50}$ (µm) | 57.46 |
| $D_{90}$ (µm) | 164.46 |
| $D_{32}$ (µm) | 22.53 |
| $D_{43}$ (µm) | 75.77 |

**Table 3.** Engine testing data using 96.4% bioethanol fuel, where $\alpha_i$ is ignition angle, $n_e$ crankshaft rotational speed, $T_e$ torque, $P_e$ power, $B_f$ fuel consumption, $b_e$ specific fuel consumption, $p_e$ mean effective pressure, $p_i$ indicated pressure, $P_i$ indicated power, $b_i$ indicated specific fuel consumption, $\eta_e$ engine efficiency and $\eta_i$ indicator efficiency

| Symbol | Unit of measurement | Original fuel supply system | Pulverizer fuel supply system |
|---|---|---|---|
| $\alpha_i$ | deg | 33 | 33 |
| $n_e$ | rpm | 3960 | 3960 |
| $T_e$ | Nm | 30.0 | 30.0 |
| $P_e$ | kW | 12.4 | 12.4 |
| $B_f$ | kg h$^{-1}$ | **14.9** | **14.58** |
| $b_e$ | g (kWh)$^{-1}$ | 1200.5 | 1176.3 |
| $p_e$ | MPa | 0.209 | 0.209 |
| $p_i$ | MPa | 0.209 | 0.209 |
| $P_i$ | kW | 23.2 | 23.2 |
| $b_i$ | g (kWh)$^{-1}$ | 642.2 | 629.3 |
| $\eta_e$ | - | 0.112 | 0.114 |
| $\eta_i$ | - | 0.209 | 0.214 |

Table 3 indicates that in the same load regime, when using small fuel drop size air-fuel mixture formed by pulverized fuel supply system, the fuel consumption decreases approximately by 2%. This can be explained by the combustion process analysis. In order to illustrate the fuel consumption decrease, Fig. 3 has been complied based on the experimental data.

Fig. 3 indicates that combustion pressure $p_{avg}$ for the pulverised fuel supply system is higher than for the regular fuel supply system. This results from the faster

combustion of the smaller fuel drop size air-fuel mixture in the cylinder. As the maximum combustion pressure $p_{max}$ for the pulverised fuel supply system has been achieved ~5 deg after top dead centre, a situation arises where the combustion pressure starts working against piston rise. From this, it can be deduced that by adjusting the ignition angle it is possible to decrease engine's fuel consumption in the current regime. Comparing the heat release rates of the regular fuel supply system and the pulveriser fuel supply system ($dQ/d\phi orig$ and $dQ/d\phi\ pulv$), it can be seen that the maximum heat release rate increases in pulverised fuel supply system approximately 13%, while in regular fuel supply system the heat release lasts longer. Thus, it can be deduced that in case of the air-fuel mixture with smaller fuel drop size, heat is released quicker and therefore, heat release is more intense. In addition, Fig. 3 shows that in case of $dQ/d\phi\ pulv$ heat release begins much earlier than with $dQ/d\phi orig$, which also causes a quick rise in combustion pressure and in the combustion velocity of the air fuel mixture in the cylinder. The heat released from the combustion process remains the same in both fuel supply systems, and is defined by the engine load.
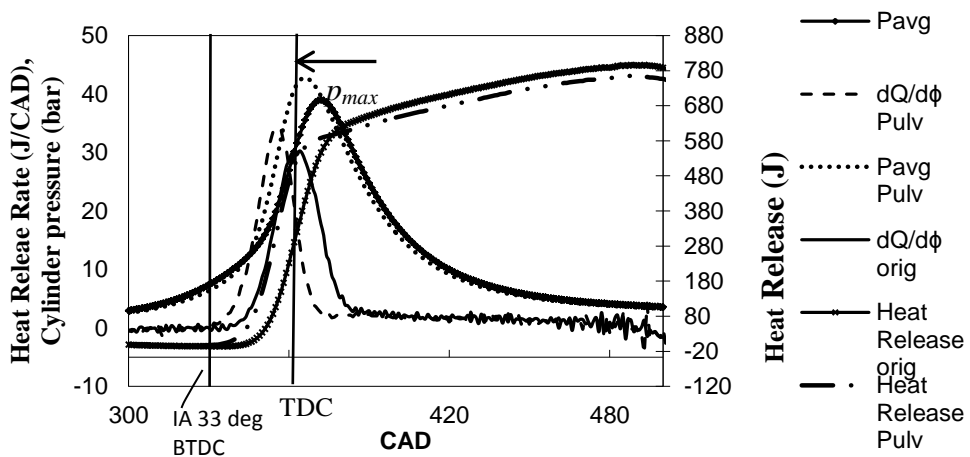


**Figure 3.** The net-heat rate emitted from the combustion process of Audi 1.8 ADR engine ($T_e$ = 30 Nm, $n_e$ = 3,960 rpm).

Based on the fuel consumption data (Table 3), the heat release rate directed into one cylinder of the engine during one working cycle (pulveriser fuel supply system $Q_{n.teor.pulv}$ = 813 J and original fuel supply system $Q_{n.teor.orig}$ = 830 J) can be calculated. By dividing the net heat released during the combustion with theoretical amount of energy in the air-fuel mixture, we get the amount of energy that was absorbed by cylinder walls. In case of the pulveriser fuel supply system, approximately ~3% more energy was absorbed than in regular fuel supply system. As more energy is absorbed by the cylinder walls, more energy will be available for the fuel drops to evaporate. Therefore, the air-fuel mixture with smaller fuel drop size evaporates faster thus causing quicker and more complete combustion of the air-fuel mixture in the cylinder.

## CONCLUSIONS

Results indicate that use of the air-fuel mixture with small fuel drop size causes an increase in combustion pressure $p_c$ and heat release $Q_n$, and therefore a decrease in engine's fuel consumption. In the current case, bioethanol consumption decreased approximately by 2%. The fuel consumption could be further decreased by optimising the ignition angle. Moreover, the air-fuel mixture with small fuel drop size causes faster evaporation, which also facilitates faster heat release and ~3% more energy absorbed by the cylinder walls.

As an extension study, it is recommended to conduct experiments with a previously adjusted engine, where the ignition angle is optimal with both air-fuel mixtures, and study the combustion of the air-fuel mixture on the engine's full load regime.

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# Transport demands in suburbanized locations

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**Abstract.** The aim of this paper is to describe the suburban residents' transport demands from the viewpoint of consumption costs in the case of regular commuting. The surveyed suburbs have different transport patterns, because these suburbs are influenced by the catchment area of the city of Prague that is a dominant city of the region, and many of the suburban settlements do not behave as traditional municipalities. Most of the existing transport links are carried out in relation to the city of Prague on radially oriented roads. The traffic intensity is often at the roads' full capacity or the roads are even congested along the ride to the city. These congestions have a negative impact on the city's environment and increase the consumption costs of passenger car transport as well. This contribution describes the transport demands based on the traffic surveys that were carried out within 15 suburban settlements during the morning peak hours and during ordinary working days. These selected settlements are located at different distances from the city and include different types of buildings and build-up areas. Thus, the authors gained a high quality sample for statistical assessment. On the basis of traffic surveys, the authors found the total amount of transport demands which were generated by selected settlements. The obtained results have proved the low competitiveness of public transport in suburban conditions from the viewpoint of travelling speed and transport costs as well, because there are no competitive advantages in this issue.

**Key words:** transit, public transport, passenger car, suburban settlement, suburbanization.

## INTRODUCTION

Designing of transport demands in a suburban location is connected to the development of suburban settlements. This trend is apparent from Western Europe in the 60s and earlier from the USA. Dislocation of settlements from urban areas brings increased automobile traffic intensity into the suburban locations. This tendency has had a negative impact on urban traffic in cities and passenger car traffic has a negative influence on public transport (transit). Furthermore, suburban bus transport began to cope with the problems caused by the growing number of passenger cars as well – it has been connected with the development of suburbanization and desurbanisation (Holmgren et al., 2008). This reason has led to the next logical step, i.e. passengers (they used the public transport until this time) have preferred passenger car transport. It could offer them better comfort than the public transport vehicles stopping in the same congestions as their cars. A passenger's decision regarding which transport mode would be used depends on the travel costs, travel time of the journey, traveling comfort, and other personal preferences (Litman, 2004; Mishalani & McCord, 2006). The final decision is the mix of the abovementioned conditions which are either

accepted or not. The role (or challenge) of transit is to offer transport within the range of acceptability for the majority of passengers and to become the best alternative. Typically, it is a compromise between travel time (or travel speed, consequently) and travel costs preferences (Litman, 2006). The dependency on usage of passenger cars is growing and is not sustainable at the current pace of growth (Lowson, 2004). Nowadays, we can see how the newly constructed high-capacity road infrastructure changes the landscape. Recreational places become multilevel crossroads or car-oriented shopping malls. This trend to build more and more high-capacity roads (since the initial transport infrastructure is not able to satisfy the increased transport demands) does not solve the problem. As it is evident from examples from many countries, systematic construction of high-capacity road transport infrastructure stimulates other transport demands of passenger cars (induced transport demands) (Small & Winston, 1999). It should be mentioned in this context that it is possible to perceive public transport usage as one of the elements to eliminate the negative impact of motorisation on the environment. The high passenger car dependence is significant especially in suburban conditions and the initial position of public transport is more difficult. The strategic goal is to perceive the public transport as competitive with passenger car transport and offer to passengers an alternative form of attractive public transport (Jakob et al., 2006).

## MATERIALS AND METHODS

The 15 localities of suburban settlements were chosen with the aim to describe the transport behaviour of suburban residents. These suburban settlements are influenced by the catchment area of the city of Prague that is a dominant city of the region. The suburban settlements were localized up to 17 km from the city of Prague (the centre). These suburbs were chosen evenly in different directions from the centre of Prague (map on Fig. 1) without direct commuter train connection, thus public transport is organised as suburban bus transport only. The suburban settlements represent different types of buildings, sizes of areas, levels of public facilities, etc. The results of the inquiries provide a wide range of data (building square, public facilities, number of households, cars, residents, etc.) for statistical processing. The traffic surveys were carried out during the morning peak hours (from 6 to 9 am) during ordinary working days. On the basis of these traffic surveys, the authors found the total amount of transport demands which were generated by selected settlements. The traffic surveys were focused on passenger car transport demands, public transport demands, pedestrians, and cyclists. The passenger car transport survey included the following items: type of car (8 classes), directionality, and occupancy. Travel time (by GPS locator) and fuel consumption of gasoline combustion engine (by fuel gauge) were measured under real conditions of traffic flow by measuring cars. The public transport surveys included the following items: directionality, travel time, departure time difference from schedule, occupancy, number of outgoing/incoming passengers, and type of fare. Travel time, time difference from schedule and occupancy were measured under real conditions of traffic flow on a public bus transport. The transport surveys were focused on evaluation of commuting from the selected suburban settlements to the city of Prague. It was sufficient to evaluate journeys from the settlements to the nearest available underground stations (public transport terminals) for the purposes of

the research – specifically to the 'Park and Ride' parking lots. These radial journeys and modal splits of all surveyed settlements are shown on Fig. 1. The traffic survey was also focused on assessment of the public transport accessibility and on the accuracy of the public transport service in the suburban settlement. Assessment of the public transport accessibility was carried out by measuring the walking distance to the bus stop within each surveyed suburb. The accuracy of the public transport (accuracy of bus connections) was assessed by the time gap between the real departure and scheduled time of departure at the bus stop. The scheduled time of departure is offered by the public transport carrier for its bus lines. This time gap was compared with the Standards of the Bus Service Accuracy, which are provided by the Regional Organiser of Prague Integrated Transport. In this context, it should be notied that all of the surveyed settlements are covered by Prague's Integrated Transport system.



**The surveyed settlements summary**

| | | | 0 2 4 | 8 | 12 | 16 | |
| --- | --- | --- | --- | --- | --- | --- | --- |

The journey to transit terminal
The underground lines
Prague's border
**The modal split**
The passenger car
The transit

**The modal split - values**

| Suburb | Tehov | Ohrobec | Bašť | Chýně 1 | Chýně 2 | Hostivice 1 | Hostivice 2 | Sulice |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Car | 100% | 92% | 90% | 85% | 84% | 83% | 81% | 80% |
| Transit | 0% | 8% | 10% | 15% | 16% | 17% | 19% | 20% |

| Suburb | Velké Přilepy 2 | Velké Přilepy 1 | Průhonice 1 | Holubice | Jenštejn | Průhonice 2 | Psáry |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Car | 76% | 76% | 76% | 75% | 72% | 69% | 54% |
| Transit | 24% | 24% | 24% | 25% | 28% | 31% | 46% |

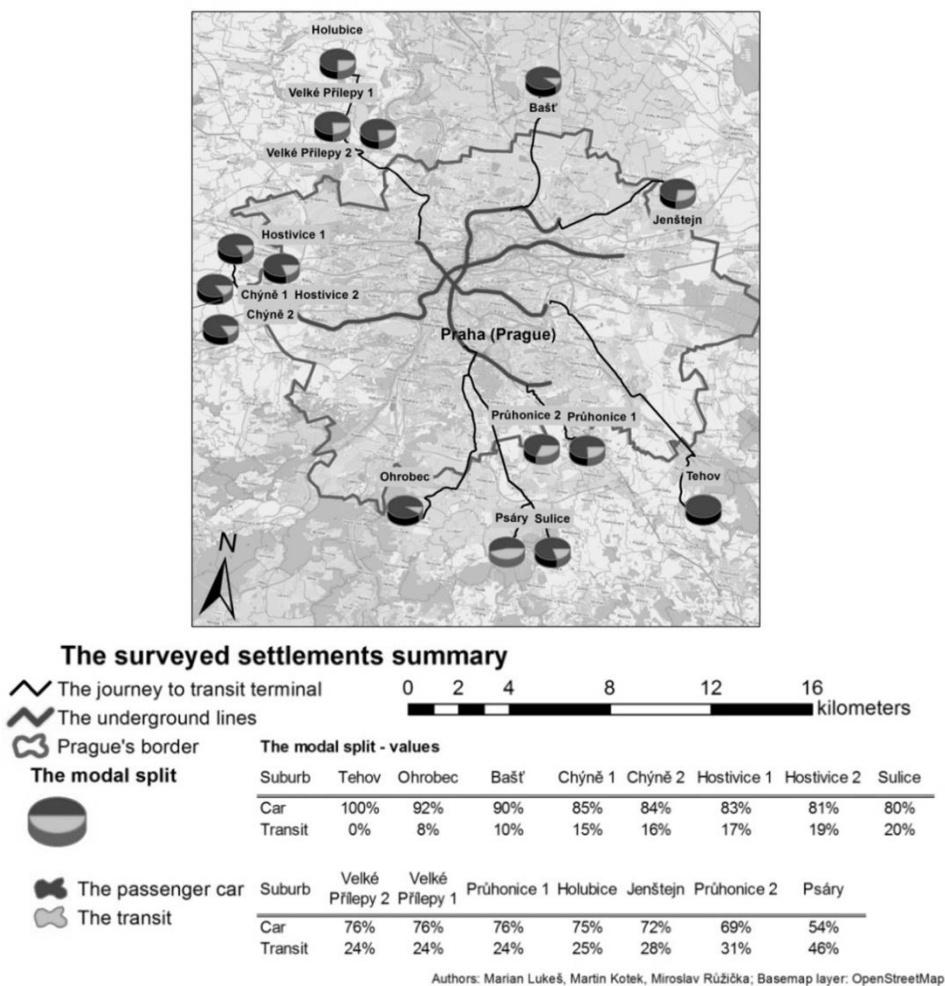Authors: Marian Lukeš, Martin Kotek, Miroslav Růžička; Basemap layer: OpenStreetMap

**Figure 1.** The modal split of the surveyed suburban settlements and the radial journeys to the city of Prague.

# RESULTS AND DISCUSSION

Accessibility of public transport has an important place in the overall view of the attractiveness of public transport, compared to passenger car transport. Fig. 2 briefly describes the distance and time of the accessibility of public transport. The minimum and maximum walking distance values provide a 'design proposal' of how to locate bus stops in the whole settlement. Usually, settlements with a low value of minimum walking distances to the bus stop (up to app. 200 m) have implemented public transport inside themselves or bus stops were used for the settlement's transport needs nearby. Other suburban settlements, where the minimum walking distances are more than app. 200 m, were built without adequate public transport provision and the residents have to use the initial bus stops which are located in the original municipality. The surveyed settlements are often located in the surroundings of original municipalities or just in the countryside; exceptionally, they are located in the centre of municipalities. A good evidence of this fact is the situation in Tehov settlement, which is located completely outside of the original municipality, but the nearest bus stop is located in the centre of the original municipality. The values of time or distance accessibility are extremely high in Tehov settlement (see Fig. 2) and due to this fact the settlement's residents do not use public transport at all. An appropriate walking or cycling infrastructure has not been built in accordance with the construction of the suburban settlement and consequently, a good level of accessibility of the public transit stop is not offered. In many suburbs, it is difficult to reach the bus transit stop by overcoming roads without the elements of pedestrian infrastructure. The roads are crossed at pedestrian crossings over the road or pedestrian crossings are missing entirely. Parents of children do not want to let their children go to the bus stop alone without adult supervising (journey to school, for hobbies, etc.). The reason is the fear of collision with a vehicle. Thus, parents transport their children by private passenger car without public transport usage. In this case, public transport is not perceived as an alternative transportation mode. This fact increases the passenger car dependence to meet the transport demands of entire families. Children accept these parental habits and bring them into their further lives (Daniels & Mulley, 2013). Fig. 2 also illustrates the fact that the appropriate locations of bus stops influence the possibility to achieve shorter walking distances and a good level of public transport's accessibility. A large total surface area of a suburb should not be an obstacle for a good level of the bus stop's accessibility, in general. This fact was also confirmed by the low value of the determination coefficient between a suburban settlement's total area and the average distance of the bus stop's accessibility ($R^2 = 0.010$). For instance, the largest of the surveyed suburban settlements covers the total area of 101 ha and it has a good level of public transit bus stop's accessibility (average time of accessibility is app. 6 minutes by walking). On the other hand, an inappropriate bus stop's location with regard to the build-up area and street structure causes very long walking distances to the bus stop within small settlements (Velké Přílepy 1 settlement only covers the total area of 14 ha). It deteriorates the accessibility of public transit and its attractiveness for passengers in the favour of passenger car transport. It can be assumed that if the average time of bus stop accessibility is about 11 minutes, passenger car usage is perceived as the time saving choice and public transit becomes uncompetitive.

Another important issue in the transit competitiveness that should be taken into account is the accuracy of public transit. Assessment of the accuracy of public transit was carried out by comparing the time gap between real departure and the scheduled time of departure. This time schedule is offered by the public transport carrier and it is publicly accessible. Subsequently, this time gap was compared with the Standards of the Bus Service Accuracy, which are provided by the Regional Organiser of Prague Integrated Transport. According to these Standards, bus connection is considered accurate if the delay is in the range of 0–179 s for intermediate bus stops and in the range 0–59 s for initial bus stop. The standard is not met if 20% of the bus connections are out of this time tolerance for accurate bus service.
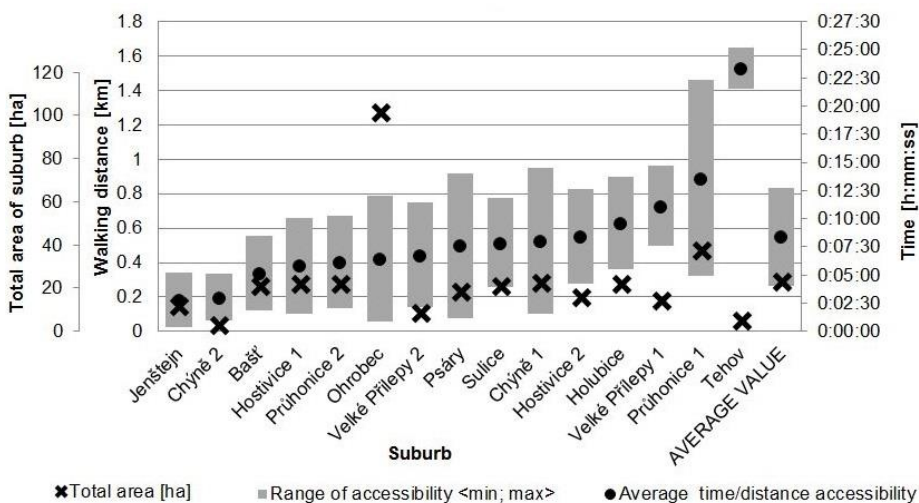


**Figure 2.** The time and distance accessibility of bus stops by walking.

From the above, it is apparent that departure of a bus connection before the scheduled time in not allowed (the so-called haste of bus connection). The obtained results have shown that only 2 surveyed settlements are on the satisfactory level of public transit accuracy (see Fig. 3) where the 'Standards of the Bus Service Accuracy' are fulfilled. In other suburban settlements, the ratio of inaccurate bus connections varies from 25–65% with regards to the offered bus connections. At this point, it should be noted that a bus stop has a guaranteed departure time in Velké Přílepy 1 settlement. Therefore, the accuracy parameter (0–179 s of delay) there should always be fulfilled. This is also confirmed by the accuracy analysis of transit connections on Fig. 4.

The results have proved a low association between offered public bus connections and the number of inaccurate bus connections by the determination coefficient ($R^2 = 0.382$), and the positive value of the Pearson's correlation coefficient has shown a positive correlation ($r = 0.618$). This fact points to a persistent problem and this problem cannot simply be solved by increasing the number of offered bus connections. It should be pointed out that the traffic survey was carried out in the morning peak hours from 6 to 9 o'clock during ordinary working days and most of the transport demands from the surveyed settlements occur during this period. The data presented in

Figs. 3 and 4 were obtained in this period as well. The accuracy analysis of the transit connections shows that the variations of haste and especially delays are high. For instance, the maximum delay reaches 18 minutes in Psáry settlement and the average value of delay is also quite high. The reason is the frequent occurrence of traffic congestions on the journey from Psáry to the city of Prague. Bus service is perceived as unreliable and therefore, consequently, with a very low competitiveness to passenger car transport. These deviations from the scheduled time are, in most cases, caused by traffic congestion on the roads. These congestions occurred in the places with lower traffic throughput than the immediate traffic intensity needs, typically intersections in the places of transition from extravilan to urban areas.
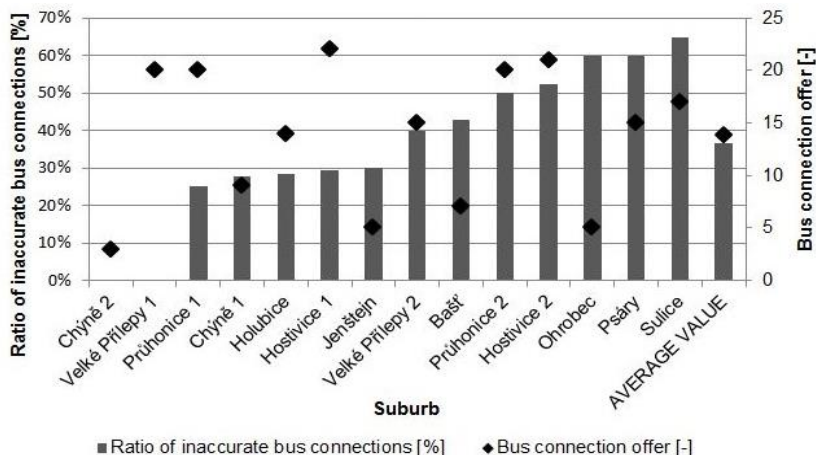


**Figure 3.** The accuracy of public transit in the morning peak hours.
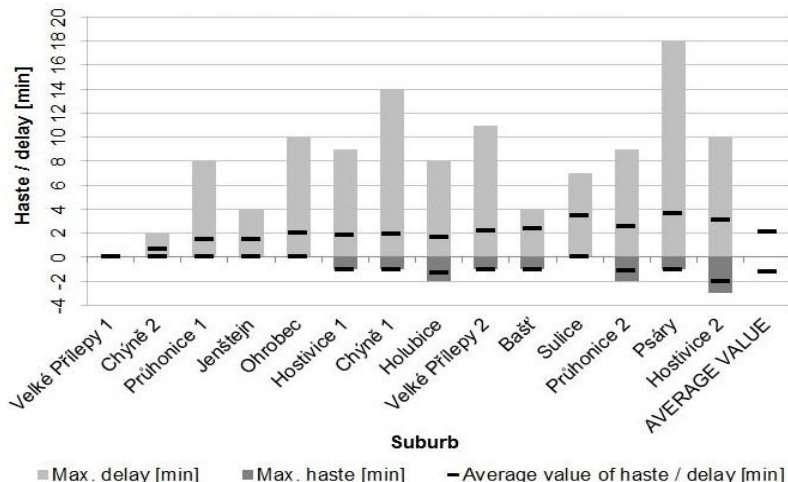


**Figure 4.** The accuracy analysis of bus connections.

The traffic surveys have proved a relationship between the public transit demand and the difference in travel costs by the determination coefficient ($R^2 = 0.630$) and the Pearson's correlation coefficient ($r = 0.794$). This difference in travel costs can be

described as a difference of consumption costs (passenger car) and quarterly pass costs (public transit) per day. Passenger car travel costs were obtained on the basis of fuel consumption under real conditions of traffic flow and were calculated at the price of € 1.36 per litre of fuel. The authors are aware that fuel consumption costs are only part of the total costs that can be included in passenger car cost calculation. But on the other hand, consumption costs have a crucial impact on the total operation cost level and describe passenger car usage more properly (Frank et al., 2008). The results were only obtained from 6 suburbs (see Fig. 5), because the authors only gained comparable data of journeys by passenger car and public transport from these suburban settlements. In this case, the pattern of transport behaviour was applied when a passenger car was shared by 2 persons (driver and passenger) for a journey from a suburban settlement to the city of Prague and back. This pattern was also compared to a long-term fare, a quarterly pass in this case, for the purposes of daily commuting. 21 working days per month were considered in this calculation, which means 42 journeys per month and equivalently 126 journeys per quarter. It was found out that the travel costs for the long-term fare (public transport) are equal or even higher than the travel costs of a passenger car shared by 2 persons (for both directions). The public transit service does not provide any competitive advantage of lower price level or better travel time in this issue. The difference between the travel costs begins to grow in the favour of public transit with the growing travel time, because the fare (especially long-term fare) is insensitive to growing travel time due to congestions.
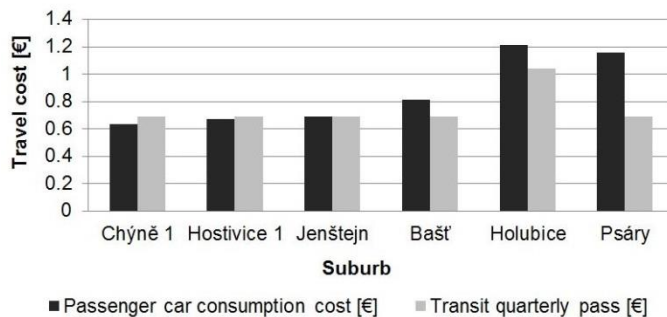


**Figure 5.** The travel costs per day – shared passenger car vs. transit.

## CONCLUSION

This paper describes the patterns of travel behaviour in suburb areas. The survey carried out confirmed the original assumption that the modal split is set in the favour of passenger car transport and the surveyed suburban settlements have high car dependence nowadays. The transport behaviour of suburban settlement residents proves strong dependence on the city of Prague, because most of the transport links are related to the city. The traffic surveys have revealed the fact that good accessibility of public transport stops does not tend to increase the public transport demand in general. Insufficient connectivity of pedestrian infrastructure is an obstacle for public transport accessibility in many cases. Walking facilities (walk-sides or paths) should be perceived as an integral part of every residential area, including suburban settlements.

It should be mentioned in this context that the potential of cycling is not fully exploited in the suburb settlements. It is necessary to perceive the suburban settlements as specific regions with different transport behaviour and patterns compared to ordinary municipalities. There are no problems with parking of passenger cars in suburban settlements or parking fees. Residents are able to find parking lots nearby their households or parking lots are included in their private plots. These unbalanced positions of the passenger car transport and transit provide an advantage of better time accessibility on the passenger cars´ side in suburban settlement conditions. Nowadays, fares and tariff system settings are not a sufficiently motivating tool for increasing public transport usage. As it has already been shown, public transport usage is stimulated by the increase of passenger car travel time and consumption costs consequently. On the other hand, the travel time of public transport is always higher than a passenger car's travel time. It would be worth to implement effective tools of public transport preference in congested parts of the journey, since transit and cars share a common road for transport nowadays and there is no perspective of a railroad being built into the surveyed settlements. This would have a beneficial effect on the fluency of public transport vehicles. In contrast, efforts to increase car travel speed tend to increase passenger car usage and this again causes the problem of congested roads without a satisfactory solution.

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# Comparison of the effect of gasoline – ethanol E85 – butanol on the performance and emission characteristics of the engine Saab 9-5 2.3 l turbo

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**Abstract.** Due to the increasing environmental demands of the European Union for reducing emissions, it is necessary to utilize biofuels at the expense of the conventional fossil fuel BA95. Biofuels in spark-ignition engines usually use ethanol at a ratio of up to 85% to 15% of the conventional fuel BA95. Such a fuel is known as E85. Butanol also has very similar properties to ethanol. Ethanol is a higher alcohol. For comparison, ethanol and butanol fuels with conventional fuels were chosen for the vehicle Saab 9-5, turbo-charged 2.3l. This vehicle is completely adapted to operation on ethanol fuel (broad adaptation control unit, suitable sealing elements, fuel pump, etc.). The engine performance and emissions were monitored when operating on these fuels as compared to the conventional fuels BA95. It can be stated that the engine reached higher performance parameters when operating on ethanol and butanol fuels. This is due to the fact that the control unit increases the fuel supply during operation on biofuels (lower calorific value of fuel). There is no lean combustion and the possible damage to the engine during long-term operation. From the perspective of bootable showing, butanol fuel has worse parameters compared to ethanol fuel and conventional fuels.

**Key words:** biofuels, butanol, ethanol, performance parameters, emissions.

## INTRODUCTION

In recent years, the European Union has devoted increasing attention to the possibility of using biofuels to power mobile machinery. The main requirement for the biofuel demand is the similarity of its chemical and physical properties to the conventional fuel.

One of the most suitable biofuels usable in internal combustion engines is bioethanol (in the Czech Republic, mainly produced from sugar beet and corn). The use of bioethanol in gasoline engines is not a significant problem and is also significantly more widespread than in diesel engines (Paul et al., 2013; Su et al., 2013). This is mainly due to the big difference between the parameters of ethanol and diesel. The main problem is the especially low ignitability (the cetane number is only 8), which must be increased with special additives. Despite significant additive dosing, it is necessary to conduct adjustments in diesel engines. First of all, increased compression ratio, used as a bi-fuel system with separate tanks and mixing bioethanol

directly into diesel (which complicates the difficult miscibility of both fuels and reduces fuel lubricity) (Křepelka, 1988; Křepelka, 1997; Hromádko et al., 2010; Hromádko et al., 2011; Küüt et al., 2011; Olt & Mikita et al., 2011; Khalil & Gupta et al., 2013).

The use of bioethanol as a fuel is not 100% normal (Shifter et al., 2013). In practice, there are usually two possibilities for adding a small amount of ethanol to gasoline (usually below 5% – the amount required for adjustment of motor management – or more typically about 85% – the number required for already adjusted motor management). The required properties of the ethanol added to motor fuels are specified in the quality standard DIN EN 65 6511 – Automotive fuels – Ethanol as a blending component for petrol – Requirements and test methods. The characteristics and requirements for E85 are given in the standard EN 65 6512 (Automotive fuels – Ethanol E85 – Requirements and test methods, 2006). Selected quality indicators of ethanol mixed in gasoline and E85 are shown in Table 1 (Šebor et al., 2006; Olt & Mikita et al., 2011).

The aim of this paper is to compare the effect of fuel on the operational characteristics of the spark ignition internal combustion engine of a vehicle Saab 9–5. It is a vehicle that is adapted to operate on biofuels, and therefore there are no technical problems arising from the aggressive nature of these fuels on the sealing elements. The chosen fuels are petrol Natural 95 (N95), 85% ethanol mixed with gasoline (E85), and butanol as a higher hydrocarbon (But). The engine control unit has a wide range of adaptation values to be able to compensate for the reduced calorific value of biofuels. The operational parameters focused on are measuring the torque, performance and emissions produced by the combustion engine.

**Table 1.** Comparison of the basic properties of ethanol, butanol and gasoline (Šebor et al., 2006; Mužíková et al., 2009; Hromádko et al., 2011)

| Fuel | Ethanol | Butanol | Gasoline |
|---|---|---|---|
| Density at 15 °C (kg m$^{-3}$) | 795 | 810 | 750 |
| Viscosity at 20 °C (mm$^2$ s$^{-1}$) | 1.52 | 3.64 | 0.4–0.8 |
| Calorific value (MJ kg$^{-1}$) | 26.4 | 32.5 | 43.3 |
| Octane number VM | 108 | 96 | 95 |
| Boiling point (°C) | 78 | 118 | 30–190 |
| Vapour pressure by Reida (kPa) | 16.5 | 18.6 | 75 |
| Oxygen content (% vol) | 34.7 | 21.6 | < 2.7 |

## MATERIAL AND METHODS

Measurements were conducted on the vehicle Saab 9-5 (Fig. 1) with a turbocharged engine of 2.3 dm$^3$. This vehicle is already adapted to run on E85 (85% ethanol and 15% natural 95). It contains sealing elements that degrade E85 fuel and an adaptive controller was used which, when using any fuel ratio of N95 E85 fuel (95 octane), sets increased supply of fuel to compensate for the difference in the calorific value of the fuel used.

The performance and emissions were measured by a cylindrical test (Fig. 2) under free acceleration. The cylindrical testing was also connected to flywheels, which slow down the dynamic process and allow the turbocharger boost pressure to develop sufficiently even at lower operating speeds.



**Figure 1.** Saab 9-5.                    **Figure 2.** Cylindrical test room.

The emission measurement used was the Brain Bee emission analyzer. The main technical parameters are given in Table 2.

**Table 2.** The parameters of the emission analyser Brain Bee

| Component | Distinction | Accuracy |
|---|---|---|
| CO | 0.01% vol. | 0.03% vol. or 5% RV (read value) |
| $CO_2$ | 0.1% vol. | 0.5% vol. or 5% RV |
| HC | 1 ppm vol. | 10 ppm vol. or 5% RV |
| $O_2$ | 0.01% vol. | 0.1% vol. or 5% RV |
| NO | 1 ppm | 10 ppm vol. or 5% RV |
| Opacity | 0.1% | 2% |
| Temperature | 1°C | 2.5°C |

Performance measurement is performed so that corresponding pulses are sensed in engine rotational speed (incremental encoders were read with speed rollers with an accuracy of 20 nanoseconds) and from them, after taking into account the transmission ratio, the angular velocity and angular acceleration of the engine crankshaft are calculated by the relationships 1 and 2.

$$\varpi_j = \frac{4 \cdot \pi}{t_j + t_{j+1}} \tag{1}$$

$$\varepsilon_j = 4 \cdot \pi \cdot \frac{\dfrac{1}{t_{j+1}} - \dfrac{1}{t_j}}{t_j + t_{j+1}} \tag{2}$$

$\varpi_j$ (rad·s$^{-1}$) – central angular speed of the engine crankshaft between j-th well plus the first turn;

361

$\varepsilon_j$ (rad·s$^{-2}$) – angular acceleration of the engine crankshaft at an angular speed $\varpi_j$; $t_j$ (s) – the duration of the j-th revolution of the engine crankshaft; $t_{j+1}$ (s) – j plus the duration of the first turn of the engine crankshaft.

The measurement begins by setting the full dose of fuel when the engine starts and quickly accelerates from idle to maximum speed. The calculation of torque and power are given by the relationships 3 and 4.

$$M = I \cdot \varepsilon \tag{3}$$

$$P = M \cdot \varpi = I \cdot \varepsilon \cdot \varpi \tag{4}$$

$P$ (W) – useful engine power to the crankshaft; $M$ (N·m$^{-1}$) – engine torque; $\varpi$ (rad·s$^{-1}$) – angular speed of the engine crankshaft; $I$ (kg·m$^2$) – moment of inertia of the moving masses at reduced engine crankshaft; $\varepsilon$ (rad·s$^{-2}$) – angular acceleration of the engine crankshaft.

A comparison of the operating parameters of the internal combustion engine vehicles Saab 9-5 were used for the fuels N95 (natural) 95 E85 (85% ethanol and 15% N95) and But (butanol).

## RESULTS

From the measurement of the performance parameters, it is evident that the highest torque and power was reached with E85. It was followed by But fuel. The worst performance parameters were achieved with the fuel N95 (Table 3, Figs. 3 and 4). This is due to the fact that the control unit increases the fuel supply during operation on biofuel (lower calorific value of fuel) to prevent lean combustion and hence possible damage to the engine during extended operation. The given results are always the moving average of 3 measurements, only in the case of the fuel But, of two measurements.

**Table 3.** Maximum engine performance parameters of Saab 9-5

|  | Max. torque (Nm) | Engine Speed (1 min$^{-1}$) | Max. power (kW) | Engine speed (1 min$^{-1}$) |
|---|---|---|---|---|
| N95 | 377 | 2,875 | 134 | 4,600 |
| E85 | 413 | 2,825 | 141 | 4,575 |
| But | 412 | 2,800 | 137 | 4,325 |

Evaluation of the emission was conducted at the same stage of the test as the measurement of the performance parameters during the acceleration tests on a cylindrical test. The emission parameters of the internal combustion engine were recorded in a text file with a frequency of 2 Hz. Evaluation then proceeded to find the emissions produced above the maximum. The minimum value was only registered in the case of $CO_2$. Thus, the values obtained are given in Table 4 below. Table 4 also

gives the maximum speed measured by a very accurate sensor that is part of the emission analyser Brain Bee.
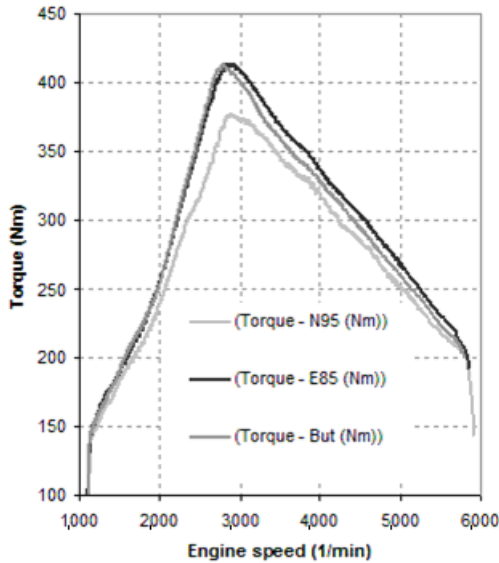


**Figure 3.** Course of engine torque.　　　　**Figure 4.** Course of engine power.
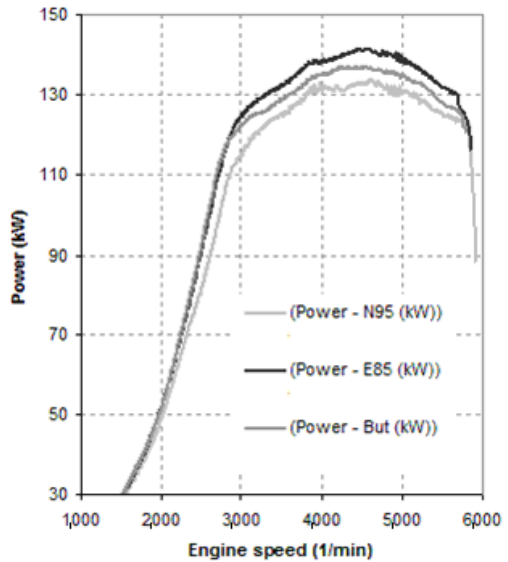
**Table 4.** Emission parameters of the engine Saab 9-5

|  |  | Speed (1/min) | $CO_2$ (%) | $NO_x$ (ppm) | HC (ppm) | CO (%) |
|---|---|---|---|---|---|---|
| E85 | 1 | 5,950 | 12.0 | 496 | 25 | 4.87 |
|  | 2 | 6,230 | 12.1 | 537 | 22 | 4.88 |
|  | 3 | 6,120 | 12.1 | 515 | 67 | 4.87 |
|  | 4 | 6,150 | 12.3 | 559 | 39 | 4.16 |
|  | Ø | **6,113** | **12.13** | **527** | **38.25** | **4.70** |
| N95 | 1 | 6,140 | 9.4 | 414 | 96 | 8.47 |
|  | 2 | 6,210 | 9.5 | 254 | 77 | 8.52 |
|  | 3 | 6,270 | 9.6 | 205 | 78 | 8.98 |
|  | Ø | **6,207** | **9.50** | **291** | **83.67** | **8.66** |
| But | 1 | 6,280 | 10.6 | 345 | 181 | 6.9 |
|  | 2 | 6,410 | 10.6 | 804 | 308 | 6.91 |
|  | Ø | **6,345** | **10.60** | **575** | **244.50** | **6.91** |

Grey colour in Table 4 underlines the average value of the fuel with which the best emission parameters are achieved. Hydrocarbons HC and carbon monoxide CO in E85 and oxides of nitrogen in the fuel N95. The graphic design of this comparison is shown in Figs. 5 and 6.
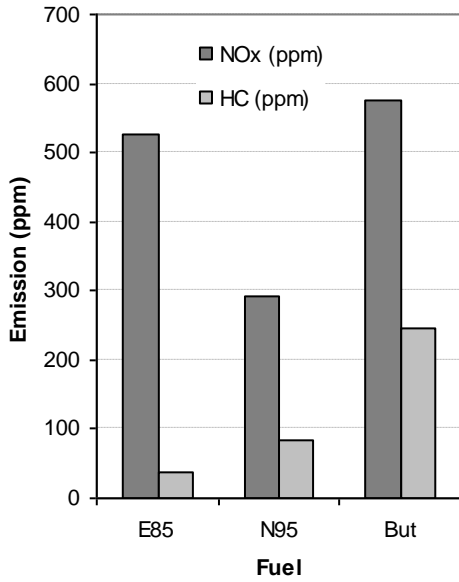
**Figure 5.** Course of emission – $NO_x$ a HC (ppm).
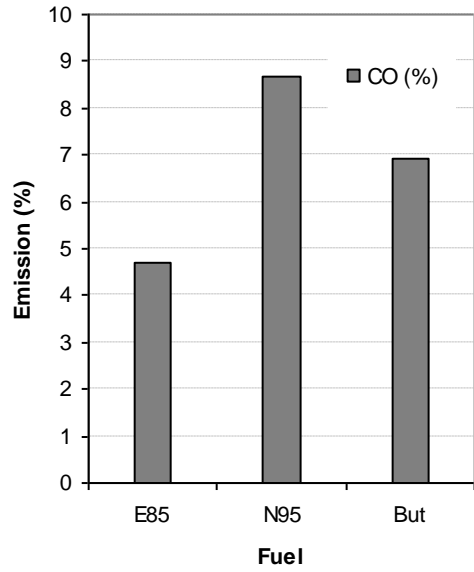


**Figure 6.** Course of emission – CO (%).

The total comparison is then shown in Fig. 7, which shows the individual components of the emission, and the summary displays the fuel in units of ppm. E85 has the best emission parameters, followed by But. The conventional fuel N95 had the worst parameters.
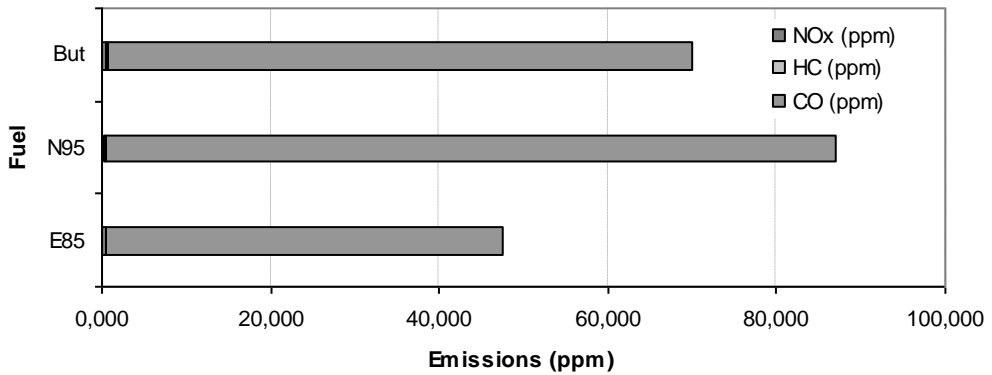


**Figure 7.** Cumulative emission – $NO_x$, HC a CO (ppm).

# CONCLUSION

Measurements were performed on a vehicle with the Saab 9–5 turbo engine capacity of 2.3 dm$^3$. It is a vehicle that allows burning of standard fuel N95, E85 biofuels, but also with increased fuel supply, so as to offset the lower calorific value of the fuel E85 to fuel N95.

The measurement used was the dynamic performance measurement while recording the emission parameters of the engine. The dynamic measurement method was implemented in the cylindrical testing, flywheels, so that the effect of the turbocharger was reached operating at low engine speeds. The analyser Brain Bee was chosen to evaluate the emission parameters.

In terms of the performance parameters, it can be stated that the abovementioned supercharged internal combustion engine achieves the best performance on the E85 fuel. The lowest performance parameters were achieved by combustion engine on the fuel N95. In terms of emissions, the order is not quite same order. The best emission parameters of the internal combustion engine were achieved when operating on E85 and worst when running on N95.

Overall, the conclusion is that the turbocharged internal combustion engine 2.3 dm$^3$ of vehicles Saab 9-5 achieved the best performance and emission parameters on the E85 fuel. The second best fuel was the fuel But, before the conventional fuel N95, which finished the testing in the third and last position.

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# The impact of biofuels and technical engine condition to its smoke – Zetor 8641 Forterra

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**Abstract:** The large number of vehicles necessitated the introduction of rules that focus in addition to traffic safety on the ecology of operation of the engine especially. Over time, the emission limits in amendments to regulations tightened, and this also applies to agriculture. One of the efforts of the EU is the introduction of biofuels precisely because, among other things, they have an impact on reducing emissions from the operation of internal combustion engines. Fatty acid methyl ester is promoted as the best substitute for diesel fuels, in the Czech conditions, namely rapeseed methyl ester (RME – Rapeseed Methyl Ester). The requirements for diesel fuel are established with the standard EN 590 and the requirements for RME with the standard EN 14 214. Efforts are made to promote replacement of the old fleet with the new. A large percentage of obsolete vehicles in poor condition still remain in use in small farms. In this paper, a comparison of a smoke combustion engine tractor Zetor 8641 Forterra when using fuels with different ratios of diesel and RME is provided. For comparison, a common test is performed in the technical emission (measurement of smoke on the principle of free acceleration). In order to assess the influence of the technical condition of an internal combustion engine and rapeseed methyl ester on smoke, gradually simulated faults of turbochargers, opening pressure and spray of pre-injection fuel injectors on a selected motor are used. The result showed that deteriorating technical condition of an internal combustion engine decreases the positive effect of rapeseed oil methyl ester blended into the fuel on smoke.

**Key words:** biofuel, smoke, technical condition of the engine.

## INTRODUCTION

In recent years, the European Union has devoted increasing attention to the possibility of using biofuels to power mobile machinery. The main requirements for biofuels include requiring similarity of its chemical and physical properties to conventional fuel.

Fatty acid methyl esters (FAME – Fatty Acid Methyl Ester) are currently promoted as the best substitute for diesel fuel, which covers most of the energy consumption of agricultural equipment. Specifically, in the Czech Republic, the most widespread substitution for diesel is Rapeseed Methyl Ester (RME) (Jokiniemi & Ahokas, 2013). The requirements for diesel fuel are established in the standard EN 590 (2010) and the requirements for RME in the standard EN 14214 (2010) (Table 1).

Based on the requirements of EU directives, it is mandatory to add RME (or other methyl esters) into diesel fuel with a maximum volume fraction of 7%. This blended fuel complies with DIN EN 590 (2010) and can be used without modification in the existing diesel engines.

**Table 1.** Comparison of the basic parameters of diesel fuel (ČSN EN 590) and RME (ČSN EN 14214)

| Request | Diesel | RME |
|---|---|---|
| Density at 15 °C (kg m$^{-3}$) | 820 to 860 | 860–900 |
| Kinematic viscosity at 40°C (mm$^2$ s$^{-1}$) | 2.0–4.5 | 3.5–5.0 |
| Freezing Point (°C) | -4 / -22 | -8 / -20 |
| Flash Point (°C) | over 55 | over 120 |
| Cetane number | min. 51 | min. 51 |
| Calorific value (MJ kg$^{-1}$) | 42,5 | 37.1–40.7 |
| Carbon residue (%) by weight | 0.10–0.30 | max. 0.3 |

In the agricultural and forestry tractors which are mainly driven by diesel engines, the exhaust pipe releases large amounts of gaseous emissions and particulate emissions into the air. These are mainly carbon monoxide (CO), carbon dioxide ($CO_2$), unburned hydrocarbons (HC), nitrogen oxides ($NO_x$), and particulate matter (PM). The negative impact of the emissions on the environment has proved the necessary for legislation to limit the amount of pollutants produced by the engine (Brožová & Růžička, 2009, Jasinskas et al., 2011). Therefore, the tractors currently marketed in the EU comply with all regulations regarding exhaust emissions.

The currently applicable legislation is based on Directive 97/68/EC (1997) and the related Directives 2004/26/EC (2004), 2000/25/EC (2000) and 2005/13/EC (2005). These Directives establish gradual tightening of the emission limits for agricultural and forestry tractors in the period from 2001–2014 in several stages (Bauer et al., 2006).

During certification, verification of compliance with the above emission limits for agricultural and forestry tractors are used in two different test cycles. NRSC (Non-Road Steady Cycle) is a measurement of the emission parameters of an engine at a steady state (Lijewski et al., 2013; Pexa et al., 2013). NRTC (Non-Road Transient Cycle) is used to measure the engine transient mode when the rotational speed and the engine load vary throughout the test cycle (Kotus et al., 2013; Pexa et al., 2013).

Emission certification ensures that no new tractor new startup exceeds the emission limits. Using a tractor, however, causes wear to all its parts, including the engine. This is reflected in the gradual increase in fuel consumption and increased emissions.

The aim of this paper is to compare the effect of different types of fuels containing biofuels and the technical condition of an engine on its smoke. For motor fuels, a 1204 Zetor 8641 Forterra (less than 100 hrs) was used successively with several mixtures (usually 6) from 100% diesel fuel to 100% rapeseed oil methyl ester. Various technical states of the internal combustion engine are simulated by changing the opening pressure of the injectors (20, 22, and 25 MPa), by change of pilot injection (7, 12, and 17°), by replacing the injectors for drain off, and a change of control of the turbocharger.

### MATERIALS AND METHODS

Measurements were carried out on the tractor Zetor Forterra 8641 with the engine 1204. The engine power at rated speed is 60 kW, the maximum torque is 351 Nm, and the specific consumption at the rated speed of 2,200 1 min$^{-1}$ is 253 g kWh$^{-1}$. In terms of design, they are inline engines with turbocharging in which the manufacturer has the

fixed smoke limit of 63.5%. Fuel is supplied into the engine combustion chamber with a transported line injection pump in the form of a single injection initiated 12° before top dead center of the piston (factory setting).

The smoke combustion engine was measured by free acceleration. This method is defined in a regulation on technical emission for assessing the technical condition of an internal combustion diesel engine. The regulation stipulates repeating of four consecutive free accelerations. In the same experiment, a smoke free acceleration method was always repeated after each 10 measurements. Usually, the first measurement was not included in the evaluation because it served to purge the exhaust system. The smoke measurement analyzer used was Brain Bee (accuracy – 2% opacity).

In our analysis of the impact of the technical condition of an internal combustion engine, the type of biofuel-using motor 1204 (motor B) located in the laboratory was used due to the ease of simulating the selected faults. Motor B serves students in practical examples and measurement. Currently, the injector, turbocharger, and tightness of the combustion chamber are mainly damaged. A 1204 motor (motor A) located in the tractor Zetor Forterra 8641 (Fig. 1) that has less than 100 hours was chosen for comparison.



**Figure 1.** Combustion engine A.          **Figure 2.** Internal combustion engine B.
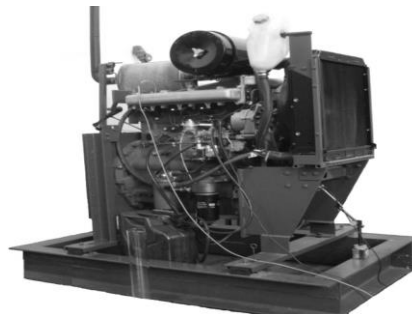
The basic parameters were the engine's fuel injector's opening pressure of 22 MPa and the pilot injection angle of 12°. In order to monitor the change in smoke due to the technical condition of the internal combustion engine, the combination of parameters given in table 2 was gradually established.

**Table 2.** Changes in parameters of the combustion engine

| Designation | Opening pressure injectors | Fuel injection | Note |
|---|---|---|---|
| 1 | 22 MPa | 12° | Engine A |
| 2 | 22 MPa | 12° | Engine A – damaged injectors of the engine B |
| 3 | 22 MPa | 7° | Engine B – damaged with leaking injector assembly |
| 4 | 22 MPa | 12° | Engine B – damaged with leaking injector assembly |
| 5 | 22 MPa | 17° | Engine B – damaged with leaking injector assembly |
| 6 | 20 MPa | 12° | Engine B – damaged with leaking injector assembly |
| 7 | 25 MPa | 12° | Engine B – damaged with leaking injector assembly |
| 8 | 22 MPa | 12° | Engine B – damaged injector with a tight fit |

The damaged injectors of the engine B (Fig. 2) are in such a state that two of the four do not have clean spray cone, but a significantly drip. The difference between tight and leaky assembly is in the use and non-use of the prescribed brass mat under the mounted injector.

Fuels were selected with the mixing ratio of 100% diesel fuel with rapeseed oil methyl ester. The mixing ratios were chosen so as to cover the entire spectrum from 100% diesel fuel to 100% rapeseed oil methyl ester.

## RESULTS

All eight changes in the condition of the combustion engine were measured for particular fuels used in the range from 100% rapeseed oil methyl ester in 100% diesel fuel 12 times. The first two measurements were always excluded from the evaluation, because there was a clean exhaust system of an internal combustion engine tractor (Table 3).

**Table 3.** Example of the measured values of smoke − 100% fuel, diesel fuel, and technical condition 1

| Order of measurement | Smoke (%) | Order of measurement | Smoke (%) |
|---|---|---|---|
| 1 – exclude | 39.6 | 7 | 32.6 |
| 2 – exclude | 34.4 | 8 | 30.0 |
| 3 | 30.9 | 9 | 30.4 |
| 4 | 30.0 | 10 | 26.5 |
| 5 | 28.8 | 11 | 28.0 |
| 6 | 33.2 | 12 | 32.0 |
| | | Ø | **30.2** |

For the final graphic design in Fig. 3, the average value has always been used. The smoke limit value specified by the manufacturer is also shown in the Figure and it reaches 63.5% smoke.
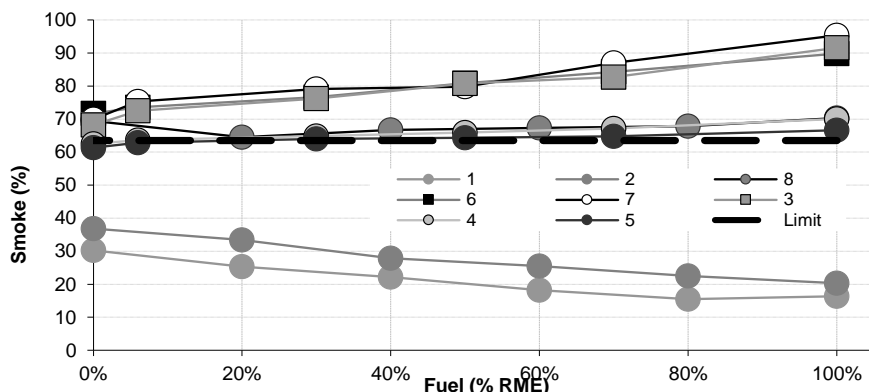


**Figure 3.** Progress of smoke depending on the technical condition of a combustion engine and the type of fuel used.

Fig. 3 shows that a combustion engine with worsened technical condition exhibits increased smokiness. Generally, however, it demonstrates that increasing share of bio-

components in the fuel reduces smoke. This was confirmed by the engine in good condition. With the deteriorating technical condition of the internal combustion engine, the positive impact of biofuels is gradually limited to a significantly degraded condition reflected in the deterioration of smoke. This is illustrated using linear interpolation on the slope of the line in Fig. 4. The slope gradually changes from negative for engine A (-14 to -17) and is moved by the gradually worsened technical state into positive territory for motor B (+ 17 to + 23).

In terms of the limit values specified by the manufacturer, smoke 63.5%, it can be stated that the motor upheld the measurement 1 and 2. In contrast, motor B essentially failed at almost any point. Only when using fuel with 100% of diesel fuel when measured, 4 and 5 were upheld by the manufacturer as specified smoke.
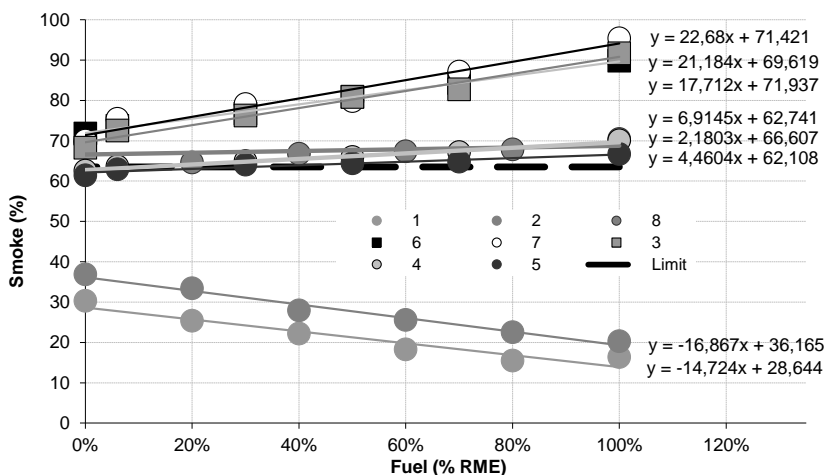


**Figure 4.** Course of smoke – the slope.

## CONCLUSIONS

We used an internal combustion engine 1204 tractor Zetor 8641 Forterra, the operating conditions of which were gradually modified in order to simulate a malfunction (the owner of engine A did not allow changes in the parameter settings and even the use of the components in engine B). At the same time, this engine used biodiesel from 100% diesel fuel to 100% biofuel (RME). The smoke of the combustion engine is the determined at each point. Originally, it was assumed that smoke of the combustion engine would decrease with a higher proportion of biofuel.

This hypothesis was confirmed only for the engine in good condition (motor A). In contrast, with the engine in poor condition (motor B – Measurement 3–8), the smoke deteriorated (Figs 3 and 4) with a higher proportion of biofuel. Increasing engine smoke was caused by damaged injector 5 to 10%, changing the opening pressure of the injectors 10 to 20%, reduction by pilot injection at 7° 10 to 20%. Most significantly, however, the increase in smoke was due to defect of the turbocharger, which caused an increase in engine smoke of about 30–60%. The initial slope of the line of the motor in good condition in the range (-14 to -17) is moved by the gradually worsened technical state into positive territory for motor B (+ 17 to + 23). It can be expected that older engines in deteriorated condition will produce more particles using a biofuels

combustion engine more than they would if they were an internal combustion engine run on clean diesel.

The disadvantage of using fuels with a higher proportion of biofuels is mainly due to the higher maintenance the fuel system (especially the removal of water from the system), lower engine performance and higher fuel consumption, based on the calorific values presented in Table 1. In contrast, the advantage of using biofuels is the higher lubricity and very good biodegradability against diesel.

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# Review of promising strategies for zero-waste production of the third generation biofuels

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**Abstract.** Biodiesel obtained from microalgae is considered a promising alternative to conventional diesel fuel. However, it has been proposed that cultivation of algae for the sole purpose of making biodiesel is neither economically efficient nor sustainable. Nevertheless, there are several ways in which microalgae can be utilized to their full potential. One possibility is to view the cultivation and utilization of microalgae as a complex process that includes wastewater treatment, carbon dioxide sequestration, production of nutritional supplements, biofuels etc. The aim of this paper is to review the most promising possibilities of combining different cultivation strategies/technologies with the coproduction of high value products (e.g. $\Omega$-fatty acids) and biofuels (algal diesel, ethanol and biogas).

**Keywords:** microalgae, microalgal biodiesel, microalgal bioethanol, coproduction.

## INTRODUCTION

Due to increasing energy demand and environmental issues associated with fossil fuels, there has been a rising interest in alternative energy sources such as solar, wind and hydro energy (Razzak et al., 2013). In the transportation sector, biomass derived biofuels have received great attention (Christenson & Sims, 2011). Biofuels have potential to replace fossil-based fuels (Pittman et al., 2011). First generation biofuels, based on vegetable oil or bioethanol, have however many disadvantages including competition with food crops for arable land, high water requirements and indirect environmental impacts from pesticide and fertilizer use (Lardon et al., 2009). Second generation biofuels from lignocellulosic biomass could address some of the issues above by utilising agricultural by-products and biomass waste however, the conversion of the biomass into ethanol is still relatively costly (Sander & Murthy 2010; Tutt & Olt 2011; Tutt et al., 2013).

Microalgae have been considered a viable biofuel feedstock. Although algae require neither arable land nor pesticides and can be cultivated in wastewater, production of algal biodiesel has received a lot of critique because of the high costs of algal biomass production and downstream processing (van Beilen 2010; Petkov et al., 2012).

In order for the microalgal production to be economically viable, it needs to be less expensive than conventional diesel fuel. Therefore, the costs of algae cultivation, biomass harvesting, and processing must be minimal (Vlysidis et al., 2011). Production of 1 kg of biodiesel requires approximately 12 kg of algal biomass (Petkov et al.,

2012). If grown in fresh water without water recycling, then an estimated 3,726 kg of water, 0.33 kg of nitrogen and 0.71 kg of phosphate is needed to produce 1 kg of biodiesel (Yang et al., 2011). Energy input for algae cultivation and downstream processing are high with current technologies. The energy used in these processes is mostly fossil fuel-derived and thus, needs to be minimized and optimized. Biodiesel from microalgae cannot be obtained at the expense of more energy than is provided by the biofuel (Scott et al., 2010). To produce feedstock sufficient for a continuous supply of biodiesel, a suitable strain of algae needs to be used. There are oil-rich algae species e.g. *Botriococcus braunii* with reported oil content up to 70% lipids, however it must be highlighted that these species grow too slowly to meet the expectation of continuous biodiesel supply (Petkov et al., 2012).

In order for microalgal biodiesel to be economically feasible, the costs of algae cultivation, biomass harvesting, and processing must be minimal. Furthermore, by-products of biodiesel refining such as glycerol as well as the residual biomass from lipid extraction must be utilised (Vlysidis et al., 2011; Zhu 2013).

Aim of this paper is to review the potential approaches and methods to make algal biofuel production economically viable and environmentally friendly by using wastewater for algae cultivation and recycling the by-products and waste.

### Algae cultivation in wastewater with $CO_2$ supplementation

In order to lower the costs of algal cultivation, wastewater could be used as a growth medium. In fact, some authors have stated that production of algal biofuels without utilising wastewater for cultivation is unlikely to be economically viable (Christenson & Sims, 2011; Pittman et al., 2011). It has been estimated that coupling wastewater treatment with biomass and biofuel production has a positive energy balance, assuming that nutrient removal with algae compensates for the cost of biological nutrient removal by 24–55% (Sturm & Lamer 2011). Furthermore, the use of wastewater as a culture medium could reduce fresh water requirement by 90% and eliminate the need for nutrients, except phosphate (Yang et al., 2011).

Conventional wastewater treatment plants use activated sludge for organic carbon, N and P removal. Activated sludge treatment is an aerobic process and requires aeration, which is energy demanding and accounts for 45–75% of a wastewater treatment plant's total energy costs. An estimated 1 kWh of electricity is needed for aeration per each 1 kg of BOD (biochemical oxygen demand) removed by activated sludge, resulting in 1 kg of $CO_2$ emissions (Razzak et al., 2013). Wastewater treatment has been estimated to consume 60 tWh of electricity per annum worldwide (Williams, 2011). Algae on the other hand do not require oxygen and have the potential to reduce the costs of wastewater treatment. A low-cost algal-bacterial wastewater treatment system has been proposed, where oxygen released from algal photosynthesis reduces the need for aeration and in return, algae utilise the $CO_2$ released by the bacteria thus, reducing the need for $CO_2$ supply (Munoz & Guieysse 2006; Cabanelas et al., 2013). Additionally, the cultivation of algae does not produce sludge by-products and allows recycling of nutrients, since microphytes incorporate nitrogen into their biomass instead of removing it in gaseous form like nitrifying/ denitrifying bacteria (Christenson & Sims, 2011; Pittman et al., 2011).

Wastewater is an abundant, nutrient rich resource. It has high concentrations of nitrogen and phosphorus, which are essential for algal growth. High load of these

elements in the discharged wastewater leads to eutrophication and may cause groundwater pollution (Christenson & Sims, 2011; Razzak et al., 2013). Urban and agricultural wastewater can be utilized for algae cultivation. The use of industrial wastewaters may be limited due to low N and P concentration and high concentration of growth-inhibiting organic contaminants and heavy metals (Munoz & Guieysse, 2006; Pittman et al., 2011).

The concentrations of total N and total P may be 10–100 mg $L^{-1}$ in municipal wastewaters and $> 1,000$ mg $L^{-1}$ in agricultural wastewaters (Pittman et al., 2011). Discharge thresholds for total N and P from urban wastewater treatment plants, established by the European Directive 98/15/EC are 10–15 mg $L^{-1}$ and 1–2 mg $L^{-1}$, respectively with a minimum removal of 80% of N and 70–80% P (DIRECTIVE, 1998). In the conventional wastewater treatment, the removal of phosphorus is particularly challenging. Species of *Chlorella* and *Scenedesmus* have been shown to effectively remove $> 80\%$ of total nitrogen and total phosphorus from secondary treated wastewater, *Chlorella vulgaris* has been shown to reduce total N and P by $> 90\%$ and 80% respectively from primary treated sewage water (Pittman et al., 2011).

Although there are sufficient nutrients in wastewater to support high algal productivity, a certain ratio of nitrogen and phosphorus is required. The optimal ratio of these nutrients is N16 : P1 and imbalance may result in growth limitation. Thus, it may be necessary to supplement the wastewater with additional nutrients (Christenson & Sims, 2011; Olguin, 2012). Additional nutrients may be supplied from anaerobic digestion effluents, which have an appropriate N/P ratio and additionally contain carbon in the form of bicarbonate (Olguin, 2012; Zhu, 2013). Nitrogen in the wastewater may be in the form of ammonia, especially in animal wastewater. Although algae can take up ammonia, high concentration of ammonia can significantly inhibit algal growth and therefore, a pre-treatment to reduce ammonia concentration in the wastewater may be required (Pittman et al., 2011; Ji et al., 2013).

*Production methods and biomass productivity*

Algae are most commonly cultured either in open pond systems or closed photobioreactors. The typical aerobic ponds for wastewater treatment are large and shallow without internal mixing, and are not optimized for algal growth (Munoz and Guieysse, 2006). A preferable alternative for nutrient circulation enhancement and increase of algal biomass productivity are high rate algal ponds (HRAP) or raceway ponds (Christenson and Sims, 2011). HRAPs are shallow, 10–30 cm deep ponds with a paddle wheel mixing system. HRAPs can treat up to 35 g BOD (biochemical oxygen demand) $m^{-2} d^{-1}$ and have a typical biomass productivity of 10–20 g $m^{-2}$ $day^{-1}$ (Munoz & Guieysse, 2006). Although high rate algal ponds are relatively inexpensive to build and operate, they require a large surface area and are prone to contamination by other protozoa, fungi and bacteria. High evaporation rate, ineffective use of $CO_2$ and poor mixing are other disadvantages for algal cultivation (Christenson & Sims, 2011).

Closed photobioreactors provide better control over temperature and evaporation, reduce the risk of culture contamination, and provide better mixing and utilization of $CO_2$. Consequently, the biomass productivity is higher compared to open ponds and range from 20 to 40 g $m^{-2}$ $day^{-1}$ (Christenson & Sims, 2011). There are several closed photobioreactor designs (Borowitzka 1999; Molina et al., 2001; Molina Grima et al., 1999; Ugwu et al., 2008), but the easiest ones to scale up are tubular bioreactors, which

have a large surface area per unit of occupied land and therefore exhibit higher efficiency of light utilization compared to other bioreactor designs (Munoz & Guieysse, 2006).

Other promising approaches for algal cultivation are immobilized cultures such as matrix-immobilized cultures and algal biofilms. Although matrix-immobilized cultures show increased lipid content and efficient nutrient removal from wastewater, the high cost of immobilization matrixes makes this approach less suitable for large scale wastewater treatment and biofuel production compared to biofilm systems (Christenson & Sims, 2011; Munoz & Guieysse, 2006). Algal productivity in a biofilm may be greater compared to suspended algae and because of simpler harvesting and dewatering operations compared to suspended algal cultures, using algal biofilms can reduce the costs of downstream processing (Christenson & Sims, 2011; Christenson & Sims, 2012). Depending on the design, algal species, water source and attachment materials used, biomass productivities between ~ 3.5 $g\,m^{-2}\,day^{-1}$ and ~75 $g\,m^{-2}\,day^{-1}$ have been reported (Gross et al., 2013). Rotating Algal Biofilm Reactors (RABR) have also been shown to sequester more total phosphorus compared to suspended reactors. RABRs can be coupled with raceway ponds for effective wastewater treatment and biomass growth. The lipid productivity and the potential fatty acid methyl ester yield in algal biofilms have been reported to be comparable with lipid productivity in suspended algae. Optimization of biofilm reactors may improve lipid productivity of such systems (Christenson & Sims, 2012).

Algal biomass productivity in wastewater depends on various factors, including the type of bioreactor used, wastewater composition and nutrient availability, illumination, pH, carbon dioxide supply etc. It has been estimated that 1,443 $m^3$ of wastewater can be treated to produce 1 ton of biomass (Feng et al., 2011a). Although the mean biomass productivity may be significant (up to 13 g dry weight $m^{-2}\,d^{-1}$) for algae grown in wastewater with high nitrogen concentration, lipid productivity may remain relatively low (< 11%) (Dalrymple et al., 2013). To induce and increase lipid production, a two phase approach has been used, consisting of a growth phase with high N concentration and a starvation phase with low nutrients concentration (Prathima Devi et al., 2012). The nitrogen deprivation enhances lipid productivity and leads toward unsaturation. Increasing lipid production via two phase approach can be applied for up-scale wastewater treatment in a cost-effective way (Prathima Devi et al., 2012).

*CO₂ supplementation and flue gas as a carbon source*

To enhance algal productivity, $CO_2$ should be supplied to the reactors. It has been estimated that at a photosynthetic efficiency of 9% microalgae could produce up to 280 tons of dry biomass $ha^{-1}\,year^{-1}$ while consuming approximately 513 tons of $CO_2$ (Sydney et al., 2010). Inorganic carbon in the water can exist in the form of $CO_2$, $HCO_3^-$, $CO_3^{2-}$ and $H_2CO_3$. In mediums with a common pH for algal growth (6.4–10.3), the dominant carbonate species is bicarbonate ($HCO_3^-$) (Van Den Hende et al., 2012, Zhao & Su, 2014). Algae can utilize $CO_2$ and $HCO_3^-$, which is converted into $CO_2$ before it can be used by Rubisco (ribulose 1.5-bisphosphate carboxylase/oxygenase) enzyme for organic compounds assimilation (Van Den Hende et al., 2012).

Flue gas from power plants and other industries, which contains up to 20% (v/v) $CO_2$, has received a lot of attention as a potential source of concentrated carbon dioxide. Although some algal species can tolerate high concentrations of $CO_2$, flue gas

also contains supplementary gases such as $SO_x$, $NO_x$ and other compounds, which can strongly inhibit algal growth (Sudhakar et al., 2011; Ono & Cuello 2003).

The inhibiting effects of $SO_2$ on algal growth are mainly attributed to the reduction in pH of the growth medium (Zhao & Su, 2014). $SO_2$ has a high solubility in water and forms $H_2SO_3$, which can be further oxidized to $H_2SO_4$. $SO_3$, also present in flue gas (2–4%), similarly forms $H_2SO_4$ (Van Den Hende et al., 2012). Moreover, the reaction of $NO_2$ with $SO_2$ forms $SO_3$, which may further reduce the pH of the medium (Van Den Hende et al., 2012). Certain levels of dissolved sulphur dioxide in the form of $SO_4^{2-}$ and $HSO_4^{-}$ have been shown to have a direct toxic effect on the algal cells (Ronda et al., 2014), although the toxicity levels of sulphur are species specific (Van Den Hende et al., 2012).

The presence of $NO_x$ (90–95% NO and 5–10% $NO_2$) is associated with changes in algal cell physiology (Zhao & Su, 2014). Low concentrations of dissolved nitric oxide form primarily nitrite ($NO_2^{-}$) in water (Ignarro et al., 1993), which can be further oxidized to $NO_3^{-}$. Both forms can be absorbed and utilised by the cells as a source of nitrogen nutrition (Chiu et al., 2011). However, concentrations higher than 300 ppm have been shown to cause a decrease in microalgal growth (Zhao & Su, 2014). Additionally, NO species (NO, $NO_2$ and very small amounts of $N_2O_2$, $N_2O_3$, $N_2O_4$, $N_2O_5$ present in flue gas) form nitrous acid ($HNO_2$) and nitric acid ($HNO_3$) in water (Van Den Hende et al., 2012). However, NO has a low solubility in water and therefore the pH effects are lesser compared to $SO_2$.

Contrarily, it has been reported that changes in medium pH and flue gas composition do not appear to affect the photochemical yield of microalgal cultures, and different microalgal strains exhibit a substantial ability to withstand a wide range of pH and flue gas composition (Olaizola, 2003). The toxic effects of $NO_x$ and $SO_x$ on algae can be overcome by using cultures with higher initial cell densities, adjusting the pH of the culture medium, or by using mutant or acidophilic algal strains (Chiu et al., 2011, Van Den Hende et al., 2012) or $SO_x$ and $NO_x$ tolerant species isolated from a close proximity of power plants (Randmann et al., 2011). Nevertheless, the use of flue gas as a carbon source for algal mass cultivation is likely to remain limited because of the inhibiting effects of $SO_x$ and $NO_x$ and additional inhibiting compounds found in flue gas such as particulate matter, halogen acids and heavy metals (Van Den Hende et al., 2012). Furthermore, the flue gas needs to be transported from the power plant to the location of algal cultivation, which would account for additional costs and indirect fossil fuel consumption (Christenson and Sims, 2011).

A more convenient source of carbon dioxide is from bioethanol fermentation and anaerobic digestion of lipid extracted algal waste biomass (Harun et al., 2009; Zhu, 2013). Recycling carbon dioxide from these sources has the potential to make algal biofuels carbon neutral.

**Harvesting**

Due to the small size of the algal cells and the relatively dilute solutions, large water volumes need to be processed to harvest the biomass. In addition to processing large flows, harvesting has to enable recycling of the separated water and needs to be time and cost effective (Jonker & Faaij, 2013). With currently used technologies harvesting and dewatering are energy consuming and have been estimated to contribute 20–30% of the total cost of microalgal biomass (Hanotu et al., 2012; Razzak et al., 2013). In this section, potentially energy and cost effective harvesting techniques are discussed.

The most common harvesting method used is centrifugation. Although centrifugation is a relatively easy method with high harvesting efficiency, it is estimated to consume from 3.3 to 4.5 MJ m$^{-3}$ of electricity and it is therefore cost-prohibitive for large scale algae harvesting (Jonker & Faaij, 2013). For suspended algal cells, tangential flow filtration has been used. However, on a large scale this method is not economically suitable because of high costs of membrane replacement and high energy requirements (Munoz & Guieysse, 2006; Christenson & Sims, 2011).

Different flotation methods have been successfully used in wastewater treatment. Flotation employs microbubbles that attach to hydrophobic particles, lifting them up to the surface where they can be collected (Hanotu et al., 2012). Flotation methods differ in the method of producing bubbles and the size of the produced bubbles. Generally, the efficiency and harvesting rate increase with decreasing bubble size. Smaller bubbles have higher surface to volume ratio and therefore a slower rising velocity, which enables better contact with the floccules (Hanotu et al., 2012).

In dissolved air flotation (DAF), water is saturated with air at a high pressure and bubbles ranging from 30 to 100 µm are formed upon realising the pressure. DAF is one of the most widely used flotation method in industrial effluent treatment (Rubio et al., 2002). This method also has a high yield of algae recovery, but is unfortunately energy intensive due to the high pressure required for air dissolution (Hanotu et al., 2012).

A less energy consuming method is the dispersed or induced air flotation, where a continuous air stream is forced through a porous material generating bubbles (Hanotu et al., 2012). Usually a high-speed mechanical agitator is used, creating bubbles 700–1,500 µm in diameter (Rubio et al., 2002). Size of the bubbles is relatively large, thus making the harvesting less effective (Hanotu et al., 2012).

Promising method for large scale algae harvesting is microflotation. Fluidic oscillator is used to produce bubbles roughly 10 times smaller and consuming 2–3 times less energy compared to DAF. Minute size of the bubbles enables effective harvesting (Hanotu et al., 2012). Unfortunately, there has been very little research regarding this method.

As individual algal cells are very small (5–50 µm), a pre-concentration step is needed prior to flotation to aggregate the small algal cells into larger floccules. Microalgal cells are negatively charged which prevents self-aggregation (Vandamme et al., 2012). In order to neutralize the cells, chemical coagulants or flocculants, typically electrolytes and synthetic polymers are used (Christenson and Sims, 2011; Hanotu et al., 2012). The most commonly used inorganic flocculants for charge neutralization are metal salts such as aluminium sulphate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$), which have a harvesting efficiency of $> 90\%$ (Vandamme et al., 2013). However, high doses of metal salts (120–1,000 mg L$^{-1}$) are required for

effective flocculation (Granados et al., 2012). Moreover, because the added flocculating chemicals remain in the harvested biomass, the use of the biomass as animal feed may be prohibited (Vandamme et al., 2013). A high concentration of metals in the biomass may also inhibit the activity of methanogenic and acetogenic bacteria in the downstream processing of the biomass (Christenson & Sims, 2011).

Alternatively natural polymers such as chitosan and cationic starches me be used as to avoid secondary pollution (Christenson & Sims, 2011; Razzak et al., 2013). Chitosan is a polymeric polyelectrolyte derived from the chitin of shellfish, which though effective, is expensive and works best at low pH values, while algal cultures require relatively high pH in the growth medium (Schlesinger et al., 2012; Vandamme et al., 2013). Positively charged cationic starches work over broader pH range and are relatively cheap (Vandamme et al., 2013). Unfortunately, cationic starches are generally less effective compared to metal salts (Granados et al., 2012). On the other hand cationic starches are not toxic and are biodegradable, which is advantageous if algal biomass production is coupled with wastewater treatment or is used as an animal feed supplement. Starches remaining in the biomass after harvesting may be hydrolysed to sugars and fermented after the lipid extraction process (Gerde et al., 2013).

In addition to natural flocculants a process referred to as autoflocculation may be used as a low cost alternative. However, the term autoflocculation is misleading, because it is a kind of chemical flocculation, which occurs in the presence of calcium or magnesium at high pH values (Vandamme et al., 2012; Wu et al., 2012). Out of the two, magnesium has been found to be more effective in flocculating freshwater algae with removal efficiency between 90 and 100% at pH 10.5–12. For a relatively safe and cost-effective increase of pH, calcium hydroxide, slaked lime and dolomite can be used (Schlesinger et al., 2012). The raise in pH also effectively kills pathogens and sterilises the biomass, which is a beneficial aspect in wastewater treatment (Vandamme et al., 2012).

Besides chemical flocculation, several physical methods have also been proposed such as electrolytic or electrocoagulation flocculation, ultrasound-aided flocculation and magnetic separation. The latter is a promising harvesting method with a cost lowering potential, which uses magnetite ($Fe_3O_4$) nanoparticles to flocculate the algal cells (Xu et al., 2011; Cerff et al., 2012). The method does not employ chemical flocculants, is rapid and relatively simple in operation and can be applied on a large scale. In addition the magnetite nanoparticles are reusable. Recovery efficiency of 95–98% was achieved depending on pH, nanoparticle dose, algal species (Xu et al., 2011) and growth medium composition. For example the presence of di- and trivalent ions such as $Ca^{2+}$, $PO_4^{3-}$ and $Mg^{2+}$ in the growth medium significantly enhances flocculation and the harvesting efficiency (Cerff et al., 2012). Although magnetic separation has been used in wastewater and water treatment systems (Zaidi et al., 2013), its application in microalgae harvesting has been limited. Further research needs to be done on the nanoparticle removal.

### Extracting high value products

Microalgae produce high value products such as omega 3 fatty acids (Ω-3), including DHA (docosahexaenoic acid) and EPA (eicosapentaenoic acid), carotenoids (e.g astaxanthin, lutein), α-tocopherol (vitamin E), and omega 6 polyunsaturated fatty acids (Ω-6) (arachidonic and γ linoleic acid) as part of their metabolism (Koberg et al., 2011). These products have use as nutraceuticals and food supplements. Algae such as *Chlorella* sp and *Scenedesmus* sp are rich in Ω-3 and Ω-6 fatty acids which can be extracted prior to lipid extraction for biodiesel production. The lipid composition of *Chlorella* sp and *Scenedesmus obliquus* are provided in table 1 (Makarevičienė et al., 2011).

**Table 1.** Lipid composition of *Chlorella* sp, *Scenedesmus obliquus* and rapeseed Makarevičienė et al., 2011)

| Fatty acids | Lipid composition (%) | | |
|---|---|---|---|
| | *Chlorella sp.* | *Scenedesmus obliquus* | Rapeseed |
| Saturated | 48.9 | 51.9 | 5.4 |
| Monounsaturated | 20.9 | 17.5 | 58.3 |
| Polyunsaturated | 23.7 | 27.4 | 36.3 |
| *Trans* isomers | 4.9 | 2.1 | |
| Omega-3 | 5.0 | 17.7 | |
| Omega-6 | 12.5 | 9.3 | |
| Linolenic | 2.3 | 10.6 | 5.0–13.0 |

According to the requirements of the Estonian Standard EVS- EN 14214, to meet the standard requirements for oxidation stability and iodine value, the contents of linolenic acid methyl ester in biodiesel fuel should not exceed 12 m/m %, polysaturated methyl ester content and polyunsaturated (4 double bonds) methyl ester content must meet the limit of 1 m/m % (EVS-EN 2012). Long-chain fatty acids with double bonds form resins the during thermo-oxidation process and therefore cannot be used in motor fuels. These fatty acids are typically saponified during the lipid conversion process and are disposed of as waste. However, the long-chain fatty acids with double bonds (including Ω-fatty acids) can be extracted prior to the production of biodiesel and sold to pharmaceutical companies for further processing. Profits from the realisation of Ω-fatty acids may have a positive effect on the overall economics of algal biodiesel production. Although the chemical company BASF has reported using headspace gas chromatography for extracting Ω-fatty acids from algal cells (BASF, 2013), there is scarce research regarding extracting valuable products from microalgae. Further research is needed to estimate the benefits and potential profits of extraction and vending of high value products from microalgae.

### Lipid extraction and conversion to biodiesel

Lipid extraction is an important step in biodiesel production and may amount up to 50% of the production cost (Goettel et al., 2013). Most lipid extraction methods require dewatering and drying of the biomass, which is energy intensive (Schlesinger et al., 2012). Thermal dewatering requires an estimated 3,556 kJ kg$^{-1}$ and therefore, improvements are needed to reduce this energy use (Sander and Murthy, 2010). Common extraction methods include mechanical pretreatment step to disrupt the algal

cells and chemical extraction using solvents. Pretreatment enhances lipid extraction and helps to reduce the amount of solvent needed. Different mechanical methods for lipid extraction have been investigated, including bead-beating, autoclaving, osmotic shock, sonication, microwaving, supercritical fluid extraction (Lee et al., 2010; Bahadar & Bilal Khan, 2013). Many of the methods above require significant biomass processing such as freezing, are time consuming and difficult to scale-up due to equipment limitations (Lohman et al., 2013). Among these, microwave radiation has been found to be more effective than others in disrupting the cells walls, resulting in higher extracted lipid yields and it can be easily scaled-up (Lee et al., 2010). A promising low-cost method for cell disruption is the application of pulse electric field, which causes cell membrane permeability. This is a low cost method that may be applied on a large scale. Additionally, it does not employ chemicals, which could contaminate or degrade the target products, and does not require drying of the biomass. Although this method is an effective pretreatment method for solvent-extraction, it does not cause the release of lipids from the cells. However, it fosters the release of other intracellular valuables and can be used for a selective extraction of pigments and enzymes, which can be collected prior to solvent extraction of the lipids (Goettel et al., 2013).

Lipids are commonly extracted using different ratios of organic solvents like ethanol, methanol, hexane, chloroform, and methylene chloride. The highest yield of lipids has been obtained using a mixture of chloroform and methanol (2:1 v/v) (D'Oca et al., 2011).

The extraction step is followed by the conversion of the extracted lipids into biodiesel. Biodiesel is a mix of fatty acid methyl esters (FAME), which are mainly produced from triglycerides (Bahadar & Bilal Khan, 2013). Transesterification is a three-step process, where triglycerides react with methanol in the presence of a catalyst to produce FAME and glycerol as final products (1–3) (Vlysidis et al., 2011):

$$\text{Triglyceride} + CH_3OH \leftrightarrow \text{FAME} + \text{Diglyceride} \qquad (1)$$

$$\text{Diglyceride} + CH_3OH \leftrightarrow \text{FAME} + \text{Monoglyceride} \qquad (2)$$

$$\text{Monoglyceride} + CH_3OH \leftrightarrow \text{FAME} + \text{Glycerol} \qquad (3)$$
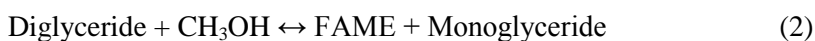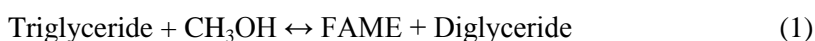
Methanol is used in surplus to shift the reaction toward the products and is recovered and recycled (Vlysidis et al., 2011). However, the high costs of extracting lipids, drying the biomass and using organic solvents make this method disadvantageous. In addition, only triglycerides can be used in the transesterification process (Takisawa et al., 2013).

Direct transesterification on the other hand, can convert phospholipids into FAME in addition to triglycerides (Takisawa et al., 2013). Supercritical methanol and ethanol have been successfully used for direct transesterification. Under supercritical conditions methanol can solvate non-polar glycerides to yield FAME and diglycerides, which are further converted into methyl ester and glycerol. This approach has a relatively short reaction time, allows the use of wet biomass, and yields maximum conversion of triglycerides into FAME (Patil et al., 2011). Microwave-mediated supercritical ethanol conditions have been shown to yield a significant amount of

biodiesel, while consuming less energy compared to conventional heating and reducing the reaction time. If converted into a continuous flow model, this method could be used for large scale biodiesel production (Patil et al., 2013). However, these methods have received a lot of critique due to energy requirements for reaching the supercritical conditions. Nevertheless, since wet biomass is used, the energy requirements may not exceed or be less than in the traditional extraction followed by transesterification method. The method can be improved by adding a co-solvent or co-catalyst, such as SrO (Koberg et al., 2011). Furthermore, utilising a power co-generation unit, direct transesterification under supercritical alcohol conditions has great potential in industrial biodiesel production (Patil et al., 2011; Patil et al., 2013).

Direct transesterification can also be achieved using acid catalysts. However, such reactions are inhibited by water. In order to use wet algal biomass, a hydrolysis using acid and base followed by direct esterification have been investigated (Takisawa et al., 2013). It has been shown that esterification of free fatty acids result in a higher FAME yield than with transesterification of triglycerides and the methylation reactions are not inhibited by water. This method has the potential to lower the cost associated with biomass drying. However, further research is necessary for it to be used on an industrial scale.

There have not been any comparative studies on the two-step (extraction followed by transesterification) and single-step (direct transesterification) biodiesel production. Since direct transesterification allows the use of wet biomass omitting biomass drying and can utilise phospholipids and free fatty acids, it may have more potential in biodiesel production. However, further research is necessary to find a suitable method which would be cost-effective and applicable on a large scale. Lipid extraction and conversion to biodiesel remains a bottleneck in algal biodiesel production.

**Utilising the waste – glycerol and lipid extracted waste biomass**
*Glycerol*
It has been proposed that in order to increase the economic sustainability of biodiesel production the by-products should be valorised. Glycerol is a common by-product of biodiesel transesterification and can amount up to 10% w/w of the biodiesel produced (Vlysidis et al., 2011). In 2010 the worldwide production of glycerol was of about 1.8 billion litres with a commercial demand of only 0.8 million per year (Cabanelas et al., 2013). Therefore most of the glycerol is discarded as waste. However, there are several ways to utilise glycerol.

Glycerol has been used for heterotrophic and mixotrophic cultivation of algae as a carbon source (Johnson & Wen, 2009; Cabanelas et al., 2013). Heterotrophic cultivation has several advantages over autotrophic cultivation, namely minimal requirements for light, a good control of the cultivation process, higher growth and better biomass harvesting (Prathima Devi et al., 2012). Adding glycerol to the culture medium has been shown to increase the saturation of fatty acids in algae, which has positive effects on the cetane number, iodine value and oxidation stability (Cabanelas et al., 2013).

Novel bio-routes to produce succinic acid for specialty chemicals and ethanol production using glycerol as a key ingredient have been explored (Vlysidis et al., 2011). Moreover, glycerol can be used for hydrogen and electricity production through microbial bioconversion (Selembo et al., 2009; Feng et al., 2011; Nimje et al., 2011;

Sarma et al., 2012). Several value-added products such as fuel bio-additives and additives for concrete can be derived from glycerol (Pagliaro et al., 2009). Additionally, glycerol can be used for co-digestion of algal waste biomass in anaerobic digestion (Ehimen et al., 2011).

### *Fermentation of lipid extracted waste biomass*

Algal biomass residuals after biodiesel refinery may account up to 65% of the whole biomass (Zhu, 2013). The lipid extracted biomass contains carbohydrates and proteins, which can be converted to bioethanol and biogas. Combining production of ethanol and methane from waste biomass with biodiesel production can improve the sustainability and lower the cost of algal biodiesel (Zhu, 2013).

Theoretically it is possible to obtain up to 0.51 kg ethanol from 1 kg of glucose (Harun et al., 2010). Based on experimental data, it has been estimated that 35 L ton$^{-1}$ y$^{-1}$ and 37.5 L ton$^{-1}$ y$^{-1}$ of bioethanol can be obtained from the carbohydrates from *Chlorella* sp. and *Botryococcus braunii*, respectively (Cabanelas et al., 2013).

Both starches and cellulose from algal cell walls can be utilised for ethanol production (Zhu, 2013). In order to extract the starches, the algal biomass has to be pretreated either mechanically or enzymatically to disrupt the cell walls (John et al., 2011). The pretreatment contributes significantly to the cost of producing bioethanol (Harun & Danquah, 2011b). However, during lipid extraction, the algal cells are typically pretreated to disrupt the cell walls and aid the release of lipids. Therefore, little or no pretreatment will be required to extract the starch from the algal biomass. Indeed, it has been shown that lipid-extracted algae yielded 60% more ethanol compared to dried and intact algae, due to polysaccharides and carbohydrates released resulting from the cell disruption during the lipid extraction (Harun et al., 2009).

Prior to fermentation, the starch and the carbohydrates from the algal cell walls including cellulose, galactose, arabinose, and xylose have to be converted into simple sugars (Harun et al., 2009). This process is called saccharification and is typically achieved with hydrolysis using acid ($H_2SO_4$), base (NaOH) or special enzymes (amylases, glucoamylases) (Harun et al., 2011; Chen et al., 2013). Unlike the plant cell walls, algal cells lack lignin and are mainly composed of cellulose, which can be converted into glucose monomers with cellulase enzymes (Harun & Danquah, 2011a; Chen et al., 2013). Following saccharification the sugars from starch and hydrolysed cellulose are fermented into ethanol using suitable yeast strains such as *Saccharomyces cerevisiae, S. uvarum, S. bayanus* etc (Harun et al., 2009; John et al., 2011).

In order to achieve maximum ethanol yield, the microalgae biomass concentration needs to be optimized. Higher biomass concentration and thus, higher carbohydrate concentration may result in release of toxic chemicals and ethanol at levels, which can inhibit the yeast cells (Harun & Danquah, 2011b). Also the appropriate temperature and pH must be maintained depending on the yeast strain used (Harun et al., 2009).

Production of bioethanol from lipid extracted biomass is an unexplored area and to date there are practically no economical assessments of this process. However, energy recovery from waste biomass is an important step in making the biodiesel production economically feasible.

*Anaerobic digestion for methane and electricity production*

The waste biomass from ethanol production may be further used as a feedstock for anaerobic digestion for biogas production and nutrient remineralisation (Sialve et al., 2009; Zhu, 2013). It has been estimated that 9,360 MJ metric$^{-1}$ ton can be recovered as methane from lipid extracted algae (Ehimen et al., 2011). However, there is scarce research on biogas production from lipid extracted and fermented algal biomass. Nevertheless, the expected value of methane recovery will be lower if residues from ethanol production are used.

The biogas yield and its methane content depends on the algal species, biomass composition, and specific conditions of the anaerobic digestion such as temperature, pH and hydraulic retention time (Passos et al., 2013). Different algal species have differences in the cell wall composition, which makes some species more readily digestible than others. Furthermore, some algae may produce extracellular compounds such as bacteriostatic (bacteria inhibiting) and bactericidal (bacteria killing) composites, which can hinder metabolic activity of the methanogenic bacteria (Mussgnug et al., 2010). Typically, the unprocessed algal biomass requires pretreatment to make the cells more accessible to the fermentative bacteria and enhance methane production. Pretreatment methods such as microwave heating (Passos et al., 2013), thermal (Marsolek et al., 2014) and pressure-thermal pretreatment (Mendez et al., 2014), and ultrasonic disintegration (Park et al., 2013) have been suggested. Effective pretreatment would reduce the hydraulic retention time and thus, the energy consumption by the anaerobic digestion tank reactor. However, as with bioethanol production, the pretreatment required is minimal if processed or lipid extracted biomass is used.

After biodiesel and bioethanol production, the residual biomass is typically poor in carbohydrates and lipids, and has relatively high protein content (Zhu, 2013). The low carbon/nitrogen ratio may result in the production of ammonia, which upon accumulation may lead to the inhibition of the bacterial flora (Prajapati et al., 2014). To lessen the release of ammonia, co-digestion with carbon rich waste, such as shredded paper waste or glycerol can be used (Ehimen et al., 2011; Prajapati et al., 2014). Moreover the addition of glycerol, a common biodiesel production by-product, has been shown to increase $CH_4$ production yields by 5–8% (Ehimen et al., 2011). The release of $NH_4^+$ can also be reduced by decreasing the fraction of unionized $NH_3$. This can be achieved by increasing the pH using high concentrations of $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ (Sialve et al., 2009).

In addition to methane, another major component of biogas is carbon dioxide (Mussgnug et al., 2010). Carbon dioxide separated from the biogas can be recycled for algal growth.

The final waste of the anaerobic digestion contains nutrients such as phosphorus and nitrogen and can be used as a fertilizer.

## OUTLOOK AND POSSIBILITIES

Choosing and optimizing suitable methods and technologies for algal cultivation and processing are of great importance to offset the costs associated with microalgal biodiesel. Ways for utilising algae are summarized in Fig. 1.

Urban and animal waste waters can be used as growth medium to reduce the cost of algae mass cultivation with the benefit of treating the wastewater. Harvesting of algae must be effective and cost-efficient. In Fig. 1, flocculation coupled with flotation has been proposed as the harvesting method, however, as the technologies develop, there may be other suitable harvesting methods.
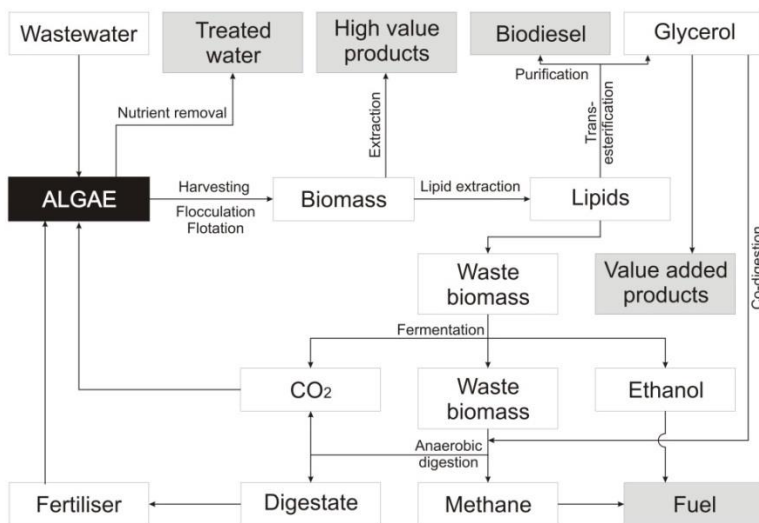


**Figure 1**. Diagram of hypothetical utilisation of algae and waste products.

Long-chain fatty acids including $\Omega$-fatty acids, which are not suitable for use as fuel and are otherwise saponified in the biodiesel conversion reactions, can be extracted prior to lipid conversion and sold to pharmaceutical companies for further purification and processing. Profits from selling $\Omega$-fatty acids and other high value products are a promising way to help balance the cost of algal biofuel. The waste biomass and by-products can be valorised and recycled. Glycerol, the main by-product of biodiesel production can be utilised in various ways, including for the production of energy and value added products. Utilising glycerol may increase the economic sustainability of biodiesel production (Vlysidis et al., 2011). The lipid extracted biomass can be further processed to obtain bioethanol and biomethane. The energy recovered from ethanol and methane production could potentially power the microalgal cultivation and processing, while the waste $CO_2$ could be re-circulated for algal cultivation (Zhu, 2013). The final waste from the anaerobic digestion can be used as a fertilizer for algal growth medium supplementation or in agriculture. This may also help to offset the total costs of the whole production chain. It has also been proposed that alternative sources of electricity such as solar and wind energy could be used *in situ* to reduce the consumption of fossil fuel-derived electricity (Collet et al., 2011).

Moreover, the algal cultivation and processing units should be located in close proximity to reduce the costs of transportation.

## CONCLUSIONS

Although the production of microalgae derived biodiesel has received a lot of criticism because of its high cost, there are possibilities to offset its high price. Using wastewater as a growth medium, utilising high value products such as $\Omega$-fatty acids and recycling the waste products may help to reduce the production cost of algal biodiesel. Further research, life cycle analysis and economical assessments are required to make algal biodiesel a sustainable fuel.

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# Composition of corncobs as a substrate for fermentation of biofuels

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**Abstract.** Lignocellulosic residues as for instance corncobs can be used as substrates for the production of biofuels. The corncobs are usually pre-treated in a thermal-physical step (steam explosion) before enzymatic hydrolysis. The pre-treatment process increases the accessibility of the raw material for the hydrolysis. The products of the hydrolyses are used as substrates for the fermentation of bio-ethanol. As an alternative, the hydrolysates could be used for the fermentation of oleaginous yeasts. These yeasts produce and accumulate lipids from glucose during growth. For the energetic use in the form of bio-diesel, the lipids can be converted into fatty acid methyl esters (FAME) in the same way as vegetable oils.

The fibre composition of the raw material was determined in regard to the proportions of cellulose, hemicellulose und lignin. It was investigated whether different corn varieties show varying compositions. The fibre compositions before the pre-treatment of ten different varieties of corncobs (from locations in Upper Austria) were determined. No significant differences were observed (cellulose: 38.8% ± 2.5%, hemicellulose: 44.4% ± 5.2%, lignin: 11.9% ± 2.3% in the dry matter).

**Key words:** corncob, fibre composition, steam explosion, biofuels, oleaginous yeasts.

## INTRODUCTION

Corncobs are an agricultural by-product which is currently used as substrate for combustion. Due to high contents of chlorine, the combustion has to take place in continuously monitored industrial power plants (Gebeshuber, 2011).

In 2012, a total of 219,702 ha (+1.2% compared to 2011) of grain maize were cultivated in Austria. The harvest was about 2,351,370 tonnes. The average yields were 10.7 t per ha. The area used for the cultivation of silage maize was 82,261 ha. Silage maize is shredded shortly after harvesting, used for silage and can therefore not be used as a substrate for biofuels (Federal Ministry of Agriculture & Environment and Water Management (Lebensministerium), 2013).

As a renewable raw material, the corncobs from grain maize are a potential feedstock for the production of biogas, biodiesel and bioethanol to fulfil the increasing demand for biofuels (Ioannidou et al., 2009). Before its use as a substrate for fermentation processes, the raw material has to be pre-treated to increase the enzymatic accessibility; for example, with the established method of steam explosion (Zimbardi et al., 2002). The lignocellulosic structure is destroyed by treatment with high temperature and saturated steam in a reactor followed by a sudden pressure decrease

(Menon & Rao, 2012), (Eisenhuber et al., 2013). Per ton of corncobs, 700 kg of mono- and oligosaccharides can be obtained by enzymatic hydrolysis. The hydrolysates of corncobs are therefore perfectly suited for biodiesel production with oleaginous yeasts. These species of oil-producing yeasts accumulate up to 50% of fat in their dry mass (Kitcha & Cheirsilp, 2011).

Corncobs are a lignocellulosic material composed of cellulose, hemicellulose and lignin. These polymeric fibres consist of monomeric molecules. Cellulose is built of C6 sugars; hemicellulose mainly of the C5 sugars xylose and arabinose. Lignin consists of phenolic macromolecules.

Cellulose, hemicellulose and lignin are embedded in a complex matrix which is very resistant to enzymatic degradation (Mosier et al., 2005; Menon & Rao, 2012). The aim of this paper was to characterize the composition of ten varieties of corncobs as raw material for the fermentative production of bio-fuels. It should be investigated whether there are significant differences, especially in regard to the proportions of cellulose, hemicellulose and lignin.

## MATERIAL AND METHODS

### Raw material

Corncobs of ten different varieties of corn (*Zea mays*) were obtained from the Austrian Agency for Health and Food Safety (AGES) (from variety of trials in Upper Austria), partially air dried at $20 \pm 2°C$ and stored in closed plastic boxes until usage. The varieties investigated for this research are not commercially available and are only grown in experimental field trials in Upper Austria. The cobs were chopped up by a garden shredder (Viking GE 260, Kufstein, Austria) to a particle size of 10 mm. The proportions of fat, protein, starch, ashes, cellulose, hemicellulose, and lignin were determined.

### Dry matter and ash content

4 g of the air dried samples were dried until constant weight at 105°C. To examine the ash contents ,the crucibles were heated at 550°C for 24 h. The masses were determined using an analytical scale (Kern 770, Balingen-Frommern, accuracy $\pm 0.00001$ g).

### Free sugars

20 g of the air-dried corncobs were grinded with a commercial coffee mill (Moulinex, Coffee Grinder, AR 100; Alençon, France). 5 g of the substance were transferred into a 25 mL reaction tube and filled with HPLC grade water to 25 g. For the extraction of soluble substances, the tubes were put into a laboratory shaker at 200 rpm for one hour. Saccharides, organic acids, ethanol, and furans were quantified using a high performance liquid chromatography (HPLC). The HPLC system Agilent Technologies, Santa Clara, 1200 Series with a Varian Metacarb 87 H column (300 * 7.8 mm) at 65°C, $H_sSO_4$ (c = 5 mmol $L^{-1}$) eluent and an isocratic flow rate of 0.8 mL $min^{-1}$ was used.

### Starch content

The starch content of the chopped corncobs was detected with the enzymatic test kit 'Total Starch Assay Kit; α-Amylase / Amyloglucosidase Method' (Megayzyme, Ireland), according to the AOAC Method 996.11 and AACC Method 76.13 (and improvements).

### Protein content

The protein content was quantified with the nitrogen determination system Dumatherm (Gerhardt, Dumas analytical system, DTM) correspondent to the ASBC-AOAC Method 997.09. Protein is detected indirectly by measurement of the total nitrogen content by combustion. The nitrogen of the sample is burned and reacts to $NO_3^-$ and is further reduced by elementary copper to form $N_2$. The $N_2$ is measured by conductivity.

### Fat content

The fat content was determined quantitatively according to the method AOAC 983.23 (Chloroform-Methanol Extraction Method, gravimetric detection).

Approximately 10 g of chopped and air dried corncobs were grinded with a coffee mill. 5 g of the grinded substrate was weighed into a round-bottomed flask. Extraction with chloroform-methanol was done in accordance with AOAC 983.23. The fat content was measured via gravimetric analysis after the extraction.

### Fibre analysis

The contents of cellulose, hemicellulose and lignin were detected gravimetrically according to the modified neutral (Neutral Detergent Fibre = NDF) and acid detergent method (Acid Detergent Fibre = ADF), adapted from the method described by Van Soest et al. (1991).

The principle of the detection of cellulose, hemicellulose and lignin is gravimetric analysis by hot filtration, extraction with organic solvents, and drying, followed by determination of the ash contents of the samples.

Quantification of Acid Detergent Lignin (ADL) was replaced by direct determination of cellulose and was conducted by hot liquid extraction with acetic acid, nitric acid, and organic solvents followed by filtration according to the method of Horwitz & Latimer (2005). For this purpose, hot liquid extraction with an acid detergent solution according to the method described by Horwitz & Latimer (2005), Neumann & Basler (1976) was performed, followed by filtration with an organic solvent.

The Hemicellulose content was calculated as the difference between NDF (cellulose, hemicellulose and lignin) and ADF. Lignin was detected indirectly by determination ADF (lignin and cellulose) and defined as the difference between ADF and cellulose.

# RESULTS AND DISCUSSION

### Fibre analysis

The contents of cellulose, hemicellulose and lignin of ten different varieties of corncobs were determined. For each of them, three repetitions of analyses were carried out. The following proportions of cellulose, hemicellulose and lignin were detected: cellulose: 38.8% ± 2.5%; hemicellulose: 44.4% ± 5.2% and lignin: 11.9% ± 2.3%).

Fig. 1 shows the percentage shares of the polymeric fibres cellulose, hemicellulose and lignin of the different varieties. The individual varieties listed on the x-axis are labelled with numbers and letters. The nomenclation of the corn varieties (origin: experimental field trials) is in accordance with the Austrian Agency for Health and Food Safety (AGES).
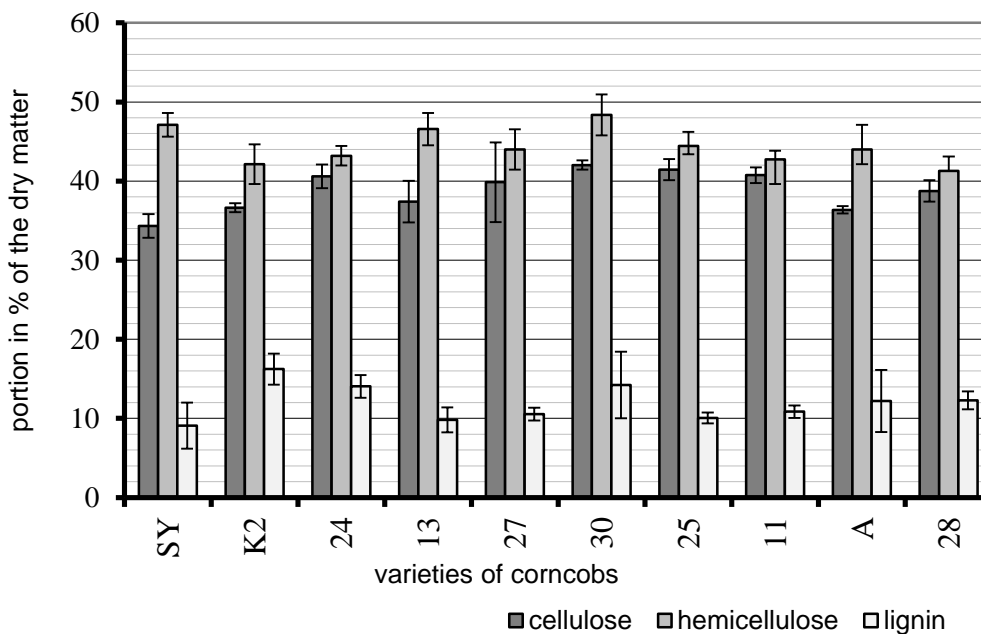


**Figure 1.** Composition of the fibres in different varieties of fresh corncobs.

In Fig. 2, the fibre contents (cellulose, hemicellulose and lignin) of ten different corncobs are visualized. The fat content was 0.3% ± 0.02 (mixture of all corncobs). The starch value in the raw material was 0.67% (m/m) ± 0.12. The protein content was 4.26% ± 0.96. The ash content was 2.88% ± 0.11 of the dry mass.
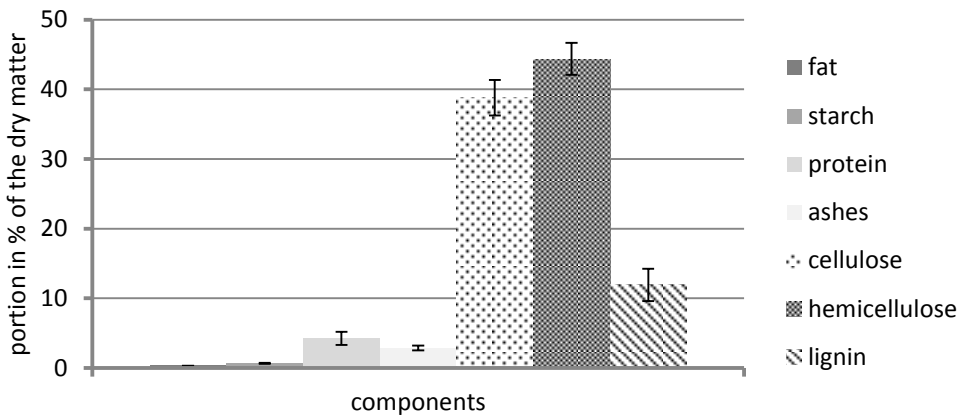
**Figure 2.** Average shares of fat, starch, protein, ashes, cellulose, hemicellulose, and lignin of the ten different varieties of corncobs tested.

## CONCLUSIONS

According to the results of the fibre analyses, there are no significant differences (significance level $\alpha = 0.05$) between the corncobs tested. Consequently, it is not necessary to choose one specific plant variety for using as a renewable energy source, namely as a substrate for the fermentation of bio-ethanol or fat by oleaginous yeasts. The polymeric fibre proportions are in accordance with the literature reviewed. The analyses published from Wang et al. indicated contents of cellulose of 40–44%, of hemicellulose of 31–33%, and of lignin of 16–18% (Wang et al., 2011). Obviously, the hemicellulose content differs from the literature and is significantly higher. For further research, it might be necessary to compare the results with another established method. Consequently, the contents of the ten different varieties of corncobs examined for this paper will be additionally compared with acid hydrolysis.

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# Utilization of urban waste in bioethanol production: potential and technical solutions

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**Abstract.** In urban forestry and greening millions of tons of lignocellulosic waste is produced every year. Although lignocellulosic materials are considered one of the most promising feedstock for the bioethanol production, biomass from urban greening and forestry goes unused. Aim of this research was to investigate the potential of such waste biomass for bioethanol production. Woody and non-woody vegetation from different sources was investigated: old and fresh leaves, and mixed waste from urban greening which contained grass, twigs, and leaves. Cellulose, hemicellulose and lignin contents in the samples were determined using fibre analysis. Dilute acid was used for pre-treatment at temperature of 130°C in order to compare yields from different methods. Thermochemical pre-treatment was followed by enzymatic hydrolysis and fermentation. Produced glucose and ethanol contents were measured using electrochemical analyser. Waste from urban greening had the highest cellulose content of 22.96% and gave the best glucose and ethanol yields, 154.5 g kg$^{-1}$ and 62.5 g kg$^{-1}$, respectively when the sample was pre-treated with dilute $H_2SO_4$. In addition, map analysis was used to assess the area manageable by urban forestry and greening in the city of Tartu to estimate the potential of greening and forestry waste as a substrate for bioethanol production that could be used as a fuel in city's public transportation system. In conclusion, it was shown that the waste from urban greening and forestry is a very promising raw material for biofuel production considering its localization and high cellulose content.

**Key words:** urban green waste, biofuel, lignocellulose, bioethanol.

## INTRODUCTION

Today fossil fuels take up 80% of the primary energy consumed in the world, of which 58% alone is consumed by the transport sector (Nigam & Singh, 2011). Continuous depletion of conventional fossil fuel reserves with increasing energy demands and climate change (Agbor et al., 2011, Nigam & Singh, 2011) have led to a move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with smaller emissions (Nigam & Singh, 2011). An attractive option to reduce fossil-fuel dependency is the use of biomass for energy production (Haberl et al., 2011). Conversion of biomass to alternative and renewable fuels is attractive potential to replace fossil-fuel-derived liquid fuels (Abdoulmoumine et al., 2012, de Almeida et al., 2013).

One of the most promising feedstock for the liquid biofuel production is lignocellulosic material (Agbor et al., 2011, Tutt et al., 2012b, Min et al., 2013, Phitsuwan et al., 2013). Lignocellulosic biomass, which is either non-edible residues of food crop production or non-edible whole plant biomass (Nigam & Singh, 2011), make up the majority of the cheap and abundant non-food materials available from plants (Naik et al., 2010, Phitsuwan et al., 2013). One of the underutilized lignocellulosic biomass resources, which is dramatically increasing with rapid urbanization worldwide, is waste from urban forestry and greening (Shi et al., 2013). This kind of biomass contains various ingredients like lawn thatches and cuttings, grass, leaves and twigs from the gardens, green roofs, and recreational parks (Kudakasseril Kurian et al., 2013). Forestry and greening waste in urban areas offers annually substantial and continuous amount of biomass (Shi et al., 2013). Additional benefits are lower feedstock cost and the ability to turn waste product into a useful commodity (Abdoulmoumine et al., 2012) that could contribute significantly to regional bioenergy system (Shi et al., 2013).

Plant biomass is primarily composed of plant cell walls of which about 75% are polysaccharides (Phitsuwan et al., 2013) that could be used for ethanol production. One possibility for new generation biofuel is production of lignocellulosic ethanol (Chiaramonti et al., 2012, Tutt et al., 2012a) which can be either used directly as fuel or mixed with gasoline in customized engines (Olt & Mikita, 2011, Haghighi Mood et al., 2013). Bioethanol is the most common biofuel in the world and it has been used as a fuel for almost century and a half. Ethanol has a high octane number, good detonation stability and high oxygen content therefore, it allows cleaner combustion process which reduces content of CO, unburned hydrocarbons and $NO_x$ in the exhaust gases (Küüt et al., 2011).

The traditional three step ethanol production process includes pre-treatment of biomass, saccharification to release the fermentable sugars from polysaccharides, fermentation of released sugars to ethanol, and finally distillation to separate ethanol (Nigam & Singh, 2011). However, the complicated structure of lignocellulosic material makes it recalcitrant to chemical and/or biological degradation (Min et al., 2013, Xu et al., 2013). To overcome this, variety of methods for pre-treatment of lignocellulosic material, including biological, physical and chemical processes but also combinations of those, have been studied (Sims et al., 2010, Agbor et al., 2011, Chiaramonti et al., 2012, Xiao et al., 2012, Min et al., 2013). Main effects of these methods are solubilisation of hemicelluloses and alteration or degradation of lignin which makes cellulose more accessible to cellulases (Sun & Cheng, 2002, Alvira et al., 2010, Sims et al., 2010, Xiao et al., 2012, Phitsuwan et al., 2013, Barakat et al., 2014). However, different types of feedstock have different cellulose, hemicelluloses and lignin contents therefore, different pre-treatments are required for particular types of biomass (Alvira et al., 2010, Phitsuwan et al., 2013).

The aim of this study was to assess the potential of the waste from urban forestry and greening as a substrate for bioethanol production using a small size town as an example (Tartu, Estonia – population ca 100,000). For the analysis of bioethanol production efficiency, different pre-treatment methods were applied to woody and non-woody vegetation from different sources in the traditional three step ethanol production process. Glucose and ethanol yields were considered to estimate the most suitable

substrate and pre-treatment method. In addition, map analysis was used to assess the area manageable by urban forestry and greening in the city of Tartu and thereby, estimate the amount of biomass available and the bioethanol production potential.

## MATERIALS AND METHODS

### Biomass

Three different kinds of biomass samples were collected to investigate the suitability of waste from urban forestry and greening for bioethanol production. Leaves were collected in two different seasons. Mixed leaves from maple, oak and bushes that were left outside over winter were collected in spring. Leaves collected in autumn consisted mainly of maple leaves. In addition waste from urban greening that contained grass, twigs, and leaves was investigated. The samples were dried to a moisture content less than 10% and ground with Cutting Mill SM 100 comfort (Retsch GmbH) and then with Cutting Mill ZM 200 (Retsch GmbH) to a particle-size 3 mm or less.

### Pre-treatment

Pre-treatment with 1% of $H_2SO_4$ solution was used to break the cell structure in the biomass and expose the cellulose to further enzymatic treatment. 1,000 mL of acid solution was added to 100 g of dried and milled biomass. Samples were heated for 60 minutes at temperature of $130 \pm 3°C$ and pressure of 3 bars. After the pre-treatment the samples were cooled to a temperature below 50°C and pH of the samples was neutralized with $K_2CO_3$ to pH range of 4.5–5.

In case of experiments where the biomass was rinsed after acid pre-treatment, the pre-treated biomass mixture was cooled to 50°C and solid fraction was separated using vacuum filtration with fabric filter (pore size 100 µm). During filtration the solid biomass was rinsed with distilled water. Distilled water was added to the rinsed biomass to regain overall mixture volume of 1,000 ml, and pH was neutralized with $K_2CO_3$ to pH range of 4.5–5.

### Hydrolysis

Enzymatic hydrolysis with enzyme complex Accellerase 1500 was used to convert cellulose in the biomass to glucose. Enzyme mixture was added to samples at a ratio of 0.3 ml per g of biomass. Hydrolysis lasted for 24 hours at a temperature of 50°C under constant stirring in rotating shaker/incubator (Unimax 1010, Heidolph Instruments GmbH & Co.KG). After the hydrolysis, the glucose concentration in all the samples was measured.

### Fermentation

In order to start the fermentation process, 2.5 g of dry yeast *Saccharomyces cerevisiae* was added to all samples. Fermentation process was carried out at room temperature under low oxygen conditions in 1,000 mL glass bottles, sealed with a fermentation tube and lasted for 5 days after which, the ethanol concentration was measured.

**Chemical analysis**

The percentage of lignin, Acid Detergent Fiber (ADF), and Neutral Detergent Fiber (NDF) in the dry mass (DM) of the biomass samples was determined at the Plant Biochemistry Laboratory of Estonian University of Life Sciences (Tecator ASN 3430; AOAC, 1990; Van Soest et al., 1991). The glucose and ethanol concentrations in the mixture were determined using Analox GL6 analyser (Analox instruments Ltd.).

**Bioethanol production potential analysis**

The area of different land cover types was measured from the Estonian Base Map distinguishing the differences between public lawn areas, parks with trees (mapped as forests in the base map), private gardens having a very similar to each other with a couple of trees, some bushes and lawn on each. Separate type of park is graveyard which in Estonia's case is mostly forest type with large old-grown trees. As the classes on the base map do not match specifics of urban green areas in detail the map was visually compared to orthophoto image of the town (as Published by the Estonian Land Board http://xgis.maaamet.ee/xGIS/XGis) and necessary corrections between different land-use classes were made considering the litter production capacity.

Also, data from municipality about the actual litter removal contracts and public green areas was used. The latter could not be used directly as it does not follow the same classification considering the litter productivity and does not cover all areas (like private gardens).

The average greening waste productivity in a square measure was estimated using data from municipality about the regularly maintained parks and public greenery areas and collected greening waste amounts from these areas.

The bioethanol production potential from Tartu greening waste was estimated from calculated yearly amounts of greening waste from different land cover types and ethanol yield. The information about city's public transportation and current biogas and diesel fuel usage was gained from local municipality and it was used to estimate the bioethanol potential as a substitute for diesel fuel in Tartu's public transportation system.

## RESULTS AND DISCUSSION

**Biomass analysis**

A biomass can be characterised on the basis of its relative proportion of cellulose, hemicellulose, and lignin (Table 1). Among the biomasses used the waste from urban greening had the highest cellulose content. Cellulose content in spring leaves is comparable to that while in autumn leaves, it is considerably lower. Lignin concentration is the highest in spring leaves. Lignin concentration in the waste from urban greening is similar to that in spring leaves while in autumn leaves it is much lower. On the other hand, the highest hemicellulose concentration was measured in autumn leaves sample. The most important property of biomass for bioethanol production is high cellulose content (Tutt & Olt, 2011) and therefore, waste from urban greening containing grass, twigs, and leaves is expected to be the most suitable substrate.

**Table 1.** The results of biomass analysis for cellulose, lignin and hemicellulose

| Sample | Hemicellulose (%) | Cellulose (%) | Lignin (%) |
|---|---|---|---|
| Spring leaves | 6.00 | 21.06 | 27.74 |
| Waste from urban greening | 6.86 | 22.96 | 22.73 |
| Autumn leaves | 8.45 | 14.54 | 11.16 |

**Ethanol production**

To evaluate the suitability of waste from urban greening and forestry for bioethanol production, samples of various types of biomass were collected and investigated. Enzymatic hydrolysis was used for the conversion of cellulose into glucose and fermentation for its later conversion to ethanol. However, the cellulose fibres are packed into the hemicellulose / lignin matrix which makes them inaccessible to enzymes. To overcome this limitation, enhance hydrolysis, and increase ethanol yield, acid pre-treatment was used to break the hemicellulose / lignin cover. Glucose yield and hydrolysis efficiency (Fig. 1) and ethanol yield and fermentation efficiency (Fig. 2) were used to characterize the effect of pre-treatment on different types of biomass.
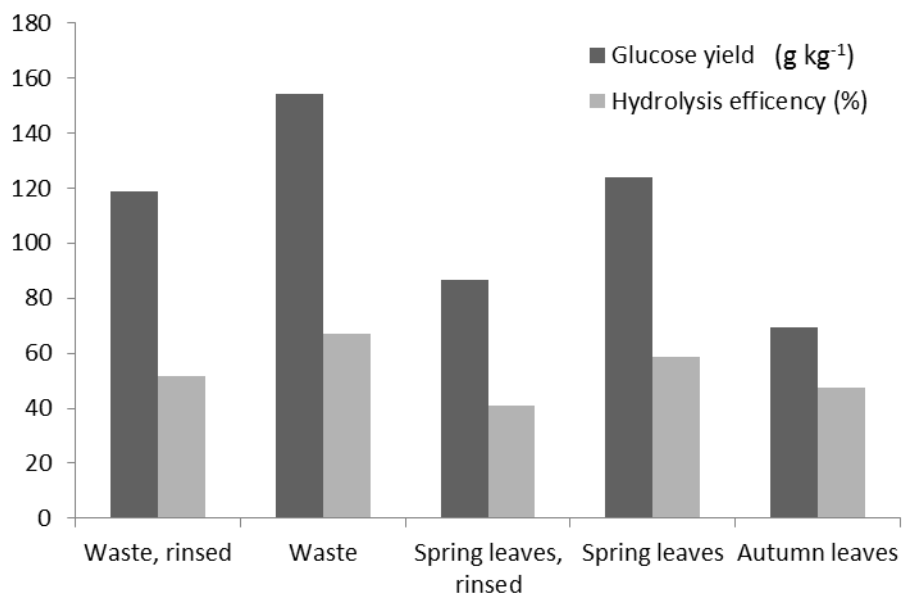


**Figure 1.** Glucose yields and hydrolysis efficiencies in case of different biomass types and pre-treatments.

Results indicate that from three types of biomasses investigated, the waste from urban greening is the best type for ethanol production. It has the highest cellulose content and resulted in the highest glucose and ethanol yields – 154.5 g kg$^{-1}$ and 62.5 g kg$^{-1}$ of biomass, respectively. Least glucose was gained from autumn leaves – 69.3 g kg$^{-1}$ that had the lowest cellulose content. Glucose and ethanol yields from

different samples depended directly on the cellulose content of the sample. The higher the cellulose content the higher the respective glucose and ethanol yields.

Hydrolysis efficiency was also the best in case of the waste from urban greening – 67.3% while the lowest result was gained with spring leaves that were rinsed with water after acid pre-treatment – 41.2%. Relatively low hydrolysis efficiency indicates inefficiency of the pre-treatment and shows that large amount of cellulose was not converted to glucose. Acid pre-treatment at these conditions did not fully degrade the hemicellulose and lignin covering from cellulose fibres and therefore, enzymes did not have good access to cellulose to degrade it to glucose.
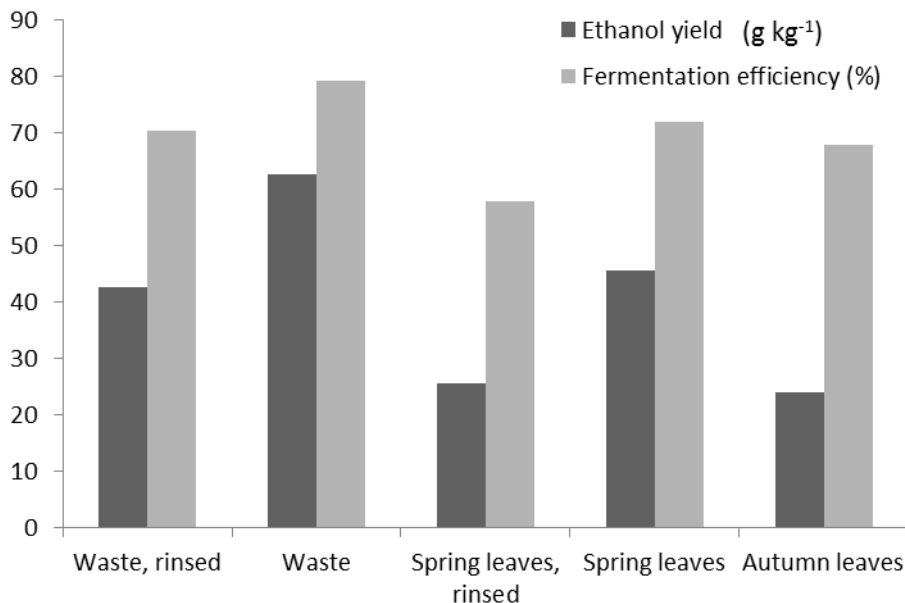


**Figure 2.** Ethanol yields and fermentation efficiencies in case of different types of biomass and pre-treatments.

Two different pre-treatment approaches were used. After the acid pre-treatment solid part of some of the samples was separated and rinsed with water before adding enzymes while other samples were immediately processed with enzymes. Rinsing of the biomass should remove by-products from the hemicellulose degradation that inhibit enzymatic activity of the yeast and thus, increase the fermentation efficiency (Tutt et al., 2012a). However, the results show that rinsing of the biomass with distilled water after acid pre-treatment decreases the glucose and ethanol yield from 154.5 g kg$^{-1}$ to 118.7 g kg$^{-1}$ and 62.5 g kg$^{-1}$ to 42.7 g kg$^{-1}$, respectively in case of waste from urban greening. Similar decrease can be seen in case of spring leaves. The lack of effect on fermentation efficiency can be attributed to low concentration of hemicellulose in all three samples. Decrease in glucose and ethanol yields was caused by the removal of some of the sugars already hydrolysed during the acid pre-treatment with rinsing water.

**Biofuel potential in the city of Tartu**

Tartu is the 2-nd largest city in Estonia with approximately 100,000 inhabitants. The city is located in south-eastern part of Estonia and its territory is 38.8 km$^2$ From this area 3.9 km$^2$ is determined as park area and public greenery and 5.1 km$^2$ consists of natural meadows and bushy areas. From the park and public greenery areas 3.15 km$^2$ is regularly maintained by the city (Tartu municipal administration, 2010). However, various kinds of verdant areas, like private yards, forest stands, graveyards, etc. which also produce greening waste are not considered in given area.

Map analysis was used in order to gain more comprehensive information about types and acreages of the green areas within Tartu city including private yards, forest stands, graveyards, etc. Various types of greeneries and park areas, estimated amounts of the greening waste they produce in a year, corresponding bioethanol potentials, and percentage of the fuel consumed by public transportation of the city that it would cover are outlined in table 2. Water-meadows, forests and railway protection zones were not includes in the estimation of these areas. Majority of the maintained greenery area in Tartu – 7.09 km$^2$ make up private gardens and courtyards. Another major part of the green area includes public greenery – 3.72 km$^2$. Park and graveyard areas however have relatively small area – 0.42 and 0.41 km$^2$, respectively. In addition, some avenues and boulevards are lined with trees which total greening area is 1 km$^2$. Also, it can be seen that not all public greeneries and parks are regularly maintained. A relatively large unmaintained green area is mostly formed by the meadows of River Emajõgi (in total exceeding the private gardens). These areas as not maintained were not included in the analysis.

**Table 2.** Comparison of various types of green areas, estimated amounts of the greening waste they produce in a year, corresponding bioethanol potentials, and percentage of the fuel consumed by public transportation of the city that it would cover based on official city records and map analysis

| Type of green area | Area (km$^2$) | Greening waste (t year$^{-1}$) | Bioethanol potential (t year$^{-1}$) | Coverage of fuel (%) |
|---|---|---|---|---|
| Public greenery | 3.72[2] | 4,285 | 268 | 21.8 |
| Private yards | 7.09[2] | 8,170 | 511 | 41.5 |
| Parks | 0.42[2] | 484 | 30.3 | 2.46 |
| Graveyards | 0.41[2] | 472 | 29.5 | 2.40 |
| Avenues | 1.00[2] | 1,152 | 72.1 | 5.85 |
| **TOTAL** | **12.64** | **1,456** | **911** | **74** |
| Regularly maintained parks and public greenery[1] | 3.15 | 3,628.7 | 227 | 18.4 |

[1] Data according to official city records (Tartu municipal administration, 2010)

[2] Data based on map analysis

During 2007–2009, the average yearly biodegradable greening waste collected from regularly maintained parks and public greeneries was 3,628.7 tons (Tartu municipal administration, 2010). Therefore, it can be estimated that approximately 1,151.9 tons of urban greening waste is produced yearly from km$^2$ of this type of area. The biomass (greening waste) potential for the city was calculated based on this estimation. For calculation of bioethanol production potential, the highest ethanol

yields gained from urban greening waste were considered – 65.2 g kg$^{-1}$ of biomass. As seen from table 2, approximately 227 tons of bioethanol could be produced in a year if all collected greening waste from regularly maintained park and public greenery area would be used for bioethanol production. Private gardens and courtyard areas have the highest biomass and bioethanol production potentials, followed by public greenery. Bioethanol production potential could be more than three times higher if greening waste collection would be extended to private gardens and courtyards. Smaller part of bioethanol potential comes also from avenues, graveyards and park areas, from which the latter are already mostly maintained and greening waste collected.

The produced bioethanol can be used as a fuel in public transportation system of the city. The buses used for local public transportation in Tartu drive yearly ca 3.5 million km and consume diesel fuel or natural gas. Currently, approximately 10% of used fuel is natural gas. The fuel consumption of buses is 40 l of diesel fuel or 41 kg of natural gas per 100 km. Therefore, it can be estimated that if only diesel fuel would be used 1.44 million litres of diesel fuel or 1.29 million litres of diesel fuel and 0.14 tons of natural gas would be necessary in a year. Since the calorific value of bioethanol is smaller than that of a regular diesel fuel – 29 MJ kg$^{-1}$ vs. 35 MJ kg$^{-1}$, respectively (Ritslaid et al., 2010), the fuel consumption of bioethanol is around 20% higher than that of a diesel fuel.

The current biogas and diesel fuel usage was taken into account when bioethanol potential as a substitute of diesel fuel in Tartu's public transportation system was calculated (Table 2). 18.4% of diesel fuel could be replaced with bioethanol if currently collected greening waste would be used to produce bioethanol. In addition 41.5% of diesel fuel could be additionally replaced with bioethanol if greening waste from courtyards and private gardens would also be processed to bioethanol. Latter would require widening the collection system to greening waste from private residences.

## CONCLUSIONS

The potential of the waste from urban forestry and greening as a substrate for bioethanol production using a small size town as an example (Tartu, Estonia – population ca 100,000) was investigated. Different pre-treatment methods were applied to woody and non-woody vegetation from different sources in the traditional three step ethanol production process. It was found that the best glucose and ethanol yields were gained with urban green waste, containing grass, twigs and leaves, pre-treated with $H_2SO_4$. The city of Tartu was analysed using remote sensing to assess the area manageable by urban forestry and greening and thereby, to estimate amount of biomass available for bioethanol production. According to public records, in years 2007–2009 Tartu had 3.15 km$^2$ of regularly maintained park and public greenery areas from where greening and forestry waste was collected. If all private garden and courtyard areas would be included in the greening waste collection system in addition to city public greenery and park areas and used for bioethanol production, more than 60% of diesel fuel used in city's public transportation could be replaced.

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# Antioxidant studies for animal-based fat methyl ester

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**Abstract.** The aim of this study was to test an antioxidant, BioSineox, for animal-based fat methyl ester, AFME, in order to determine the optimal concentration of this antioxidant for meeting the six-hour oxidation stability requirement as set in the EN 14214:2010 standard. Oxidation stability was measured using a Biodiesel Rancimat 873, which meets the requirements of the EN 14112 standard. The variety of raw materials used in the production of methyl esters, i.e. biodiesels, renders a variety of fatty acid profiles. Consequently, the reaction of biodiesels with various antioxidants must be individually tested for each combination. Before the antioxidant is added during the manufacturing process, it must be tested in laboratory conditions. As the main result of this study it can be stated that the process requires a relatively high (2,000 ppm) BioSineox concentration in order for the biodiesel to meet the six-hour oxidation stability requirement. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum. To reach this target, the concentration of the antioxidant must be further increased.

**Key words:** Antioxidant, biodiesel, methyl ester, oxidation stability, Rancimat.

## INTRODUCTION

The interest in biofuels as engine fuels is increasing in both developing and industrialized countries. The trend covers many engine applications from transport to agricultural mechanization and electricity production. The growing interest in biofuels correlates to increasing energy consumption, a decline in crude oil resources and hence the obligation to replace fossil fuel products, the obligation to reduce greenhouse gas (GHG) emissions, and the desire to improve energy self-sufficiency by utilizing waste-derived feedstock in distributed energy production – often managed by minor local companies (Sidibé et al., 2010).

Accordingly, in the year 2007 the EU set an ambitious target for increasing the use of renewable energy sources to 20% of the total energy consumption, as well as for increasing the energy efficiency to 20% in comparison with the baseline scenario under development in the EU by 2020. Also, the share of biofuels in transportation shall be increased to 10% (The EU Climate and Energy Package, 2011). In 2014, the EU's framework 2030 presents even more ambitious targets; the green house gas emissions should be decreased 40% below the 1990 level and the renewable energy consumption

should increase up to 27% of the total energy consumption by 2030 (The European Commission, 2014).

To achieve this target, even smaller-scale production of biofuels requires further attention and development. Biodiesels produced from oils and fats through the transesterification reaction with alcohol is one of the smaller-scale alternatives needed on a national level to maximize overall energy production and efficiency. The optimal raw material for the production of biodiesel is waste or non-edible oil.

In Finland, biodiesel production is focused on certain raw materials, such as rapeseed oil, animal fat and spent edible frying oil. In particular, increasing attention has been placed on the manufacture of waste-derived fuels in order not to compete with food production when promoting biofuel launching.

In the Ostrobothnia region of Finland, in the surroundings of the city of Vaasa, animal fat containing waste is widely used as feedstock for biofuels. The production of animal-based fat methyl ester, AFME, studied in the current project, does not compete with food production. Much to the contrary, the utilization of waste feedstock for fuels reduces environmental loading, since the uncontrolled decomposition of wastes in landfills is avoided (Lagus, 2010). According to Cooper (Cooper, 2010) the $CO_2$ production per megajoule is very low for waste animal oil biodiesel.

In many respects, biodiesel is similar to fossil diesel fuel, which poses a great advantage. Its potential as an alternative fuel for compression ignition engines is significant. The production and processing of biodiesel is, however, not always sufficiently controlled, and thus the fuel's chemical and physical properties may vary depending on the adopted feedstock and thermal parameters, as well as on the chemical components applied to develop the final product. The various processes involving oils and fats produce fuels with varying compositions and properties (Knothe, 2010; Varde & Veeramachineni, 2011).

In order to replace fossil fuel consumption by biodiesel, the latter must be of good quality and meet the requirements set in the EN 14214 standard. The oxidation stability limit has proven to be one of the most difficult requirements to fulfill and is thus an obstacle for the widespread commercialization of biodiesels. In March 2013, the standard EN 14214:2010 was replaced by the EN 14214:2012. One of the changes was an increase in the oxidation stability requirement from 6 hours minimum to 8 hours minimum.

Several studies have indicated that even the six-hour oxidation stability could not be reached without the addition of an antioxidant (Chen et al., 2011; Karavalakis et al., 2011; Vauhkonen et al., 2011). The increase of the six-hour requirement to a minimum of eight hours aims to ensure the usability of biodiesel as a blending component in fossil diesel grades, a part of paraffinic diesel fuels, as well as pure diesel fuel even after prolonged storage times (AGQM, 2010; AGQM 2011).

Resulting from the wide variety of biofuel origins and manufacturing processes, the properties and suitability of each fuel have to be studied individually. The paucity of data on animal fat based fuels also calls for examining such new fuel options that may be of importance in promoting distributed energy production and self-sufficiency of farms, local communities, and factories.

In this study, the oxidation stability of AFME was determined in dependence on antioxidant concentration. Several measurements were conducted. The main targets were to further the work of a local biodiesel producer and to gather additional general

information about biodiesel antioxidants. Antioxidant concentrations are usually relatively high which increases the overall costs of biodiesel production. Testing several antioxidants aims at finding an antioxidant that would improve oxidation stability to the desired level in the smallest possible concentration. The results presented in this paper were measured in the end of the year 2011 and in the beginning of 2012. At the time, the desirable oxidation stability level for biodiesel was still 6 hours and it was therefore used as the target when the optimum antioxidant concentration was determined.

## MATERIAL AND METHODS

### Samples

The examined animal-based fat methyl ester was produced by Feora Ltd in Nykarleby, Finland. Feora Ltd is a Finnish animal feed company that commenced biodiesel production in 2010. Feora produces ester-type biodiesel using a two-stage process that combines acid-catalyzed esterification and alkali-based transesterification. The product is mainly used as heating fuel and as fuel in non-road engines (Bengts, 2010).

### Antioxidants

The tested antioxidant was BioSineox[TM] Liquid, a product of Antioxidant Aromas and Fine Chemicals Ltd, KZN, South Africa. It is a synergistic blend of hindered phenolic compounds with a chemical name of mixed butylated hydroquinones (Fig. 1). The major components are MTBHQ (mono t-butyl hydroquinone) and DTBHQ (2.5-di-tert-butylhydroquinone) (AAFC, 2009).
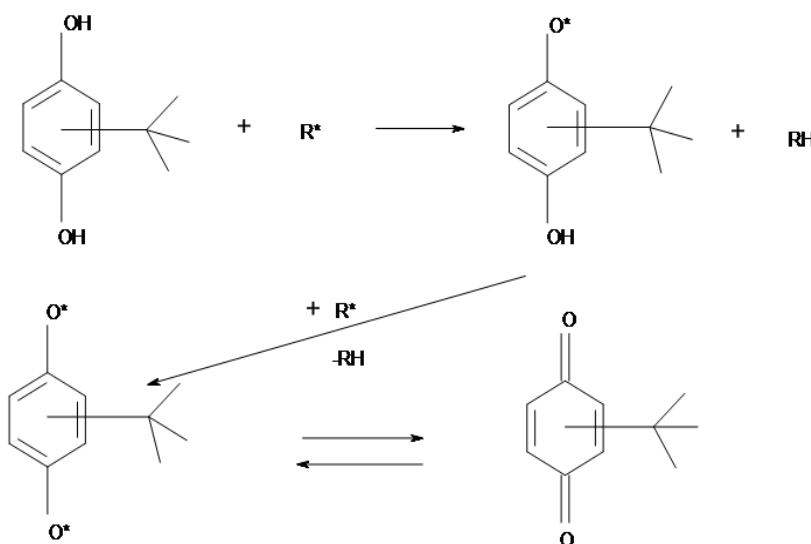


**Figure 1.** Tert-Butylated hydroquinones form a stable electron structure by donating two H atoms. Forming resonance stabilizes the structure (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

In general, hindered phenols work best in biodiesels produced from any kind of raw material, and butylated hydroquinones are said to work best in biodiesels produced

from vegetable feedstock. Biodiesel is prone to oxidation depending on the raw material it has been produced from. Various raw materials have a variety of fatty acid profiles. The higher the unsaturation level is, the more reactive and unstable the resulting biodiesel becomes, thus requiring a higher antioxidant concentration in order to be stabilized. (Antioxidant Aromas & Fine Chemicals /Pty Ltd, date not available).

Feora previously used the Ionol BF 1000 antioxidant, a product of Degussa Sant Celoni, S.A., Spain, in the production of biodiesel. Ionol BF 1000 contains a blend of butylated phenolic compounds (Oxiris Chemicals S.A., 2009). The concentration of this antioxidant in production was rather high, 2,000 ppm. The new BioSineox[TM] Liquid antioxidant was tested to determine whether a smaller dosage would prove sufficient for biodiesel to reach the six-hour limit in a Rancimat test.

**Experimental**

Two types of samples were sent to the University of Vaasa (UV) by Feora Ltd, i.e. biodiesel samples containing the antioxidant and samples without the antioxidant, both obtained directly from the production process. In the following text, the term 'blank sample' is used to refer to samples that were obtained before the addition of the antioxidant. The term 'process sample' refers to samples obtained directly after the addition of the antioxidant during the production process (Fig. 2). Moreover, in the laboratory at UV, 'laboratory samples' were prepared by adding various amounts of the antioxidant into the blank or process samples provided by Feora Ltd. The preparation of the laboratory samples began with the blending of the antioxidant into blank-sample biodiesel to achieve a final antioxidant concentration of 10 m/m%, i.e. the stock solution. The laboratory samples were then prepared using the stock solution and left to react in room temperature (20°C) for at least one day prior to taking measurements. During this time, the samples were shaken by hand several times. The mixing was performed at random time. The reaction times for the measurement sets varied because it was assumed that a few days difference would not have an effect on the obtained results.
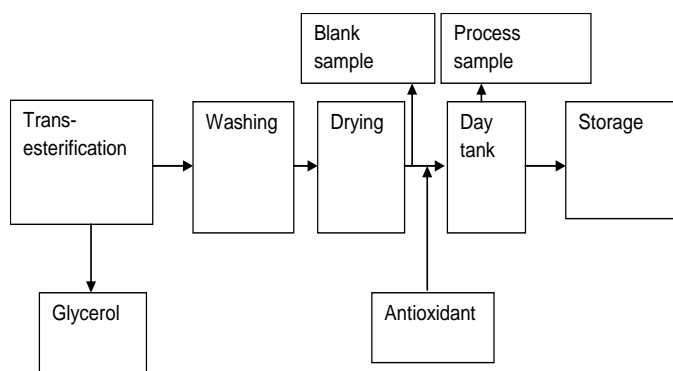


**Figure 2.** Process diagram of antioxidant addition in the production process (Oxiris Chemicals, 2009).

The oxidation stability of biodiesels was studied using a Biodiesel Rancimat 873 instrument (Metrohm, Herisau, Switzerland), which meets the required EN 14112

standard (European Committee for Standardization, 2003). The air flow rate was set at $10\,l\,h^{-1}$, using 3.00 grams of a sample ($\pm$ 0.01 g) placed in the equipment's heating block at a temperature of 110°C. The vapors coming from the sample were directed into a measuring flask containing 50 ml of distilled water. The conductivity of the water was recorded by a computer. The induction times of the biodiesel samples were determined. Several sets of measurements were made for AFME with various concentrations of the antioxidant (Fig. 3). The measurements were repeated for all of the samples and the presented results show the mean values of these two parallel measurements.
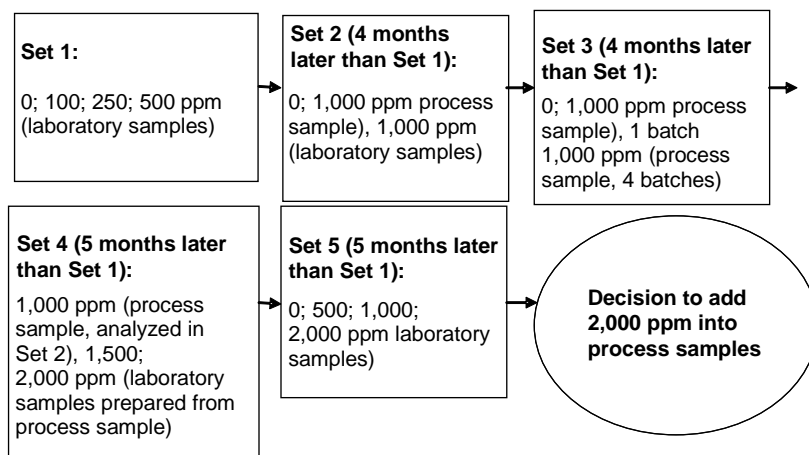
| Set 1:<br><br>0; 100; 250; 500 ppm (laboratory samples) | Set 2 (4 months later than Set 1):<br><br>0; 1,000 ppm process sample), 1,000 ppm (laboratory samples) | Set 3 (4 months later than Set 1):<br><br>0; 1,000 ppm process sample), 1 batch 1,000 ppm (process sample, 4 batches) |
|---|---|---|
| Set 4 (5 months later than Set 1):<br><br>1,000 ppm (process sample, analyzed in Set 2), 1,500; 2,000 ppm (laboratory samples prepared from process sample) | Set 5 (5 months later than Set 1):<br><br>0; 500; 1,000; 2,000 ppm laboratory samples | **Decision to add 2,000 ppm into process samples** |

**Figure 3.** Diagram of the measurement sets, the schedule and the samples.

In addition to oxidation stability, certain other properties of the biodiesel-antioxidant mixtures were measured for some of the samples. These properties are presented in Table 1. The purpose was to detect whether the addition of the antioxidant would alter certain properties of the AFME biodiesel. Measurements were carried out for a blank sample and a sample containing 500 ppm of the BioSineox antioxidant. The biodiesel for both the blank and the 500 ppm sample was obtained from the same production batch.

The water content was determined with a Karl Fischer Coulometer Mettler Toledo C30 according to the EN ISO 12937 standard. The iodine value and the acid value were measured according to the EN 14111 and EN 14104 standards, respectively. Both measurements represent titration methods that were performed employing a Mettler Toledo DL 70 ES titrator. The surface tension was measured with a Tensiometer TD 2 Lauda according to the manufacturer's instructions. The trace elements were measured using an ICP-OES Perkin Elmer Optima 7000 DV according to the EN 14538 standard and the manufacturer's instructions.

## RESULTS AND DISCUSSION

**Table 1.** Properties of animal-based fat methyl ester, blank sample (without antioxidants), and laboratory sample containing 500 ppm of BioSineox

| Property (unit) | Limit, EN 14214 | AFME, blank | AFME, 500 ppm, BioSineox |
|---|---|---|---|
| Water content (ppm) | ≤500 | 510 | 430 |
| OSI (h) | ≥6 | 2.5 | 6.5 |
| Iodine value (g $I_2$ 100 $g^{-1}$) | ≤120 | 77 | 76 |
| Acid value (mg KOH $g^{-1}$) | ≤0.50 | 0.15 | 0.17 |
| Surface tension (mN $m^{-1}$) | - | 30.0 | 30.9 |
| Mg+Ca (mg $kg^{-1}$) | ≤5.0 | <1.0 | <1.0 |
| Na+K (mg $kg^{-1}$) | ≤5.0 | <1.0 | <1.0 |
| P (mg $kg^{-1}$) | ≤10.0 | 0 | 0 |

As Table 1 shows, oxidation stability reflects the most significant difference in performance between the blank and the 500 ppm sample. The BioSineox antioxidant improved the oxidation stability of the tested biodiesel by 160%, while other properties showed only minor changes. The water content of the 500 ppm antioxidant sample appeared to reduce by 15% in comparison with the blank sample. This may have resulted from a change in the chemical structure, as a number of chemical compounds interfere with water determination.

The first Rancimat measurements were carried out for an AFME series of four laboratory samples containing 0 (blank), 100, 250 and 500 ppm of the BioSineox antioxidant. The results are presented in Fig. 4. The error bars in Fig. 4, (as well as in Figs 5 and 6) are drawn based on the relative standard deviation, 4.5%, measured for this method earlier. The six-hour limit was reached when 500 ppm of the antioxidant was added. It should be noted that the blank sample with 2.5 h yielded relatively high oxidation stability. Normally, the oxidation stability of AFME samples containing no antioxidants measures approximately 0.6 h.

In the second set of measurements, a blank sample was compared to a process sample and a laboratory sample, both containing 1,000 ppm of BioSineox. The Rancimat result for the blank sample was 0.6 h. The Rancimat result for the 1,000 ppm process sample was 3.2 h, while the 1,000 ppm laboratory sample yielded 27 h oxidation stability.

In the third set of oxidation stability measurements, a blank sample was compared to two process samples containing 1,000 ppm of the antioxidant. The process samples consisted of biodiesel from a single production batch and a mixture of four batches, respectively. The blank sample yielded an oxidation stability index of 0.6 h, whereas the one-batch sample reached 2.4 h and the four-batch sample 2.2 h oxidation stability.

The 1,000 ppm process sample analyzed in the laboratory in the second set of measurements had previously yielded a result of 3.2 h. When the sample was reanalyzed, oxidation stability had declined to 2.7 h. Four weeks had elapsed since the initial measurement. Two more laboratory samples were produced from this 1,000 ppm process sample by adding the BioSineox antioxidant to final concentrations of 1,500 ppm and 2,000 ppm, respectively. The results for both of the new samples

exceeded the six-hour limit. The result for the sample containing 1,500 ppm reached 7.1 h and for the sample containing 2,000 ppm 12 h (Fig. 5).
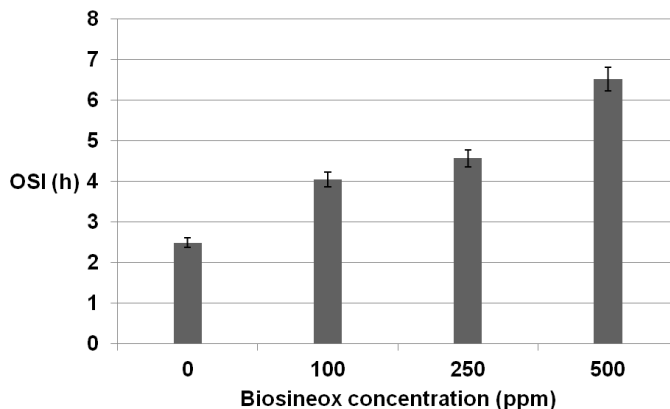


**Figure 4.** Measured oxidation stability indexes (h) for methyl ester samples containing different concentrations between 0 and 500 ppm of the BioSineox antioxidant.
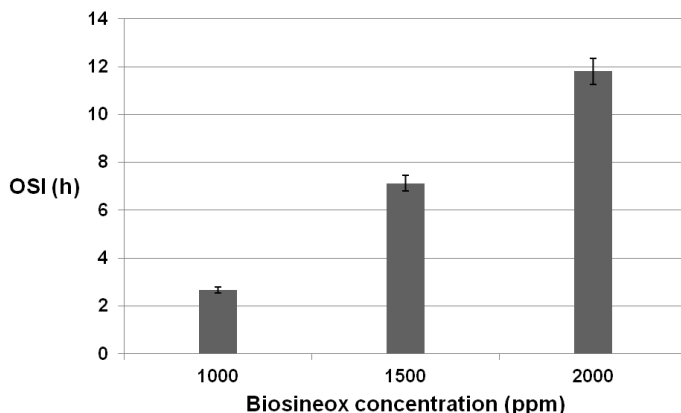


**Figure 5.** Measured oxidation stability indexes (h) for methyl ester samples containing concentrations of 1,000, 1,500 and 2,000 ppm of the BioSineox antioxidant.

In the final series of analysis, biodiesel samples were prepared in the laboratory containing the antioxidant at concentrations of 0, 500, 1000, 1,500 and 2,000 ppm. The results are presented in Fig. 6.

The blank sample rendered an oxidation stability of 0.6 h, corresponding to the results from the two earlier blank samples. Also, the OSI for the 1,000 ppm process sample was comparable to earlier results. However, the results for the 500 ppm, 1,500 ppm and 2,000 ppm laboratory samples proved lower than the previous results for these concentrations. While the 2,000 ppm sample reached 57% (Fig. 5), the 500 ppm and 1,500 ppm samples equaled the previous OSI results (Figs 4 and 5) only by 12% and 19%, respectively. One possible explanation for this contrastive outcome is that the samples in Fig. 6 were allowed a shorter reaction time than the samples of

413

Fig. 5. The earlier samples (Fig. 5) were prepared in the laboratory by adding the antioxidant to a process sample that already contained 1,000 ppm of the antioxidant. The first antioxidant addition had already been carried out in the process line four weeks prior to the measurements.
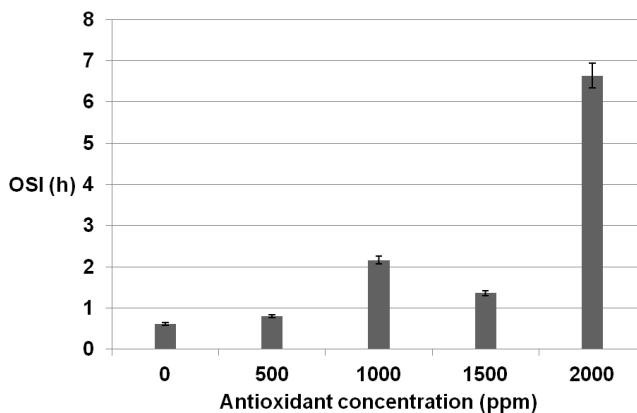


**Figure 6.** Measured oxidation stability indexes (h) for methyl ester laboratory samples containing different concentrations between 0 and 2,000 ppm of the BioSineox antioxidant.

As for the final series, the samples (Fig. 6) were prepared four days later than the 10 m/m % stock solution, and the samples were analyzed one day after preparation. It is probable that the mixtures of biodiesel and the antioxidant were allowed for an insufficient amount of time to blend and react properly.

The first laboratory samples yielded higher OSI results with lower antioxidant concentrations. A 500 ppm addition of BioSineox sufficed to exceed the six-hour level. The blank sample also yielded a relatively high result, 2.5 h, while the later blank samples yielded only 0.6-hour results. This, along with variation of the raw material, may help explain the smaller amount of the antioxidant reaching the desired level of biodiesel oxidation stability. The promising result that lower concentrations of the antioxidant had achieved high enough oxidation stability for some of the laboratory samples cannot overcome the fact that concentrations of 2,000 ppm were required in process samples.

Some studies on vegetable oil based biodiesels have indicated that lower concentrations of antioxidants suffice to reach the desired six-hour level. According to Chakraborty and Baruah (Chakraborty & Baruah, 2012) a concentration of 500 ppm of the TBHQ (tert-butylhydroxyquinone) antioxidant achieved the limit of six hours for a vegetable oil based biodiesel from *Terminalia belerica*, while a biodiesel sample containing no antioxidant reached oxidation stability of 3.8 h. According to the same study, the PY (pyrogallol) and PG (propyl gallate) antioxidants efficiently rendered the six-hour result with a concentration of only 100 ppm. Ruy (Ruy, 2010) has examined the effect of an antioxidant on soybean oil based biodiesel. With the concentration of 100 ppm, the addition of TBHQ resulted in oxidation stability of more than six hours and the concentration of 2,000 ppm yielded oxidation stability exceeding 40 hours. However, Ruy discovered that the BHA (butylated hydroxyanisole) and BHT

(butylated hydroxytoluene) antioxidants helped oxidation stability meet the specification at the 1,000 ppm level (Ruy, 2010). Altogether, these results underline what was previously mentioned, i.e. an antioxidant's efficiency may vary depending on the raw material. Thus, all of the antioxidants and raw materials require individual examining.

The requirement for high antioxidant concentrations has also been observed in studies that have examined certain antioxidants used in the production of AFME. For instance, the Ionol BF 1000 antioxidant has previously been used in the production of biodiesel. The results for BioSineox and AFME mixtures reported here and those for Ionol BF 1000 treated methyl esters presented by Vauhkonen et al. (2011) show that the antioxidant concentrations must be at least 2,000 ppm for these antioxidants to reach the OSI limit of six hours (Vauhkonen et al., 2011). The low reproducibility of the results in this study necessitates further research in order to ensure a sufficient OSI in general and for AFME in particular.

## CONCLUSIONS

In the current study, the BioSineox antioxidant was added to animal-based fat methyl ester in order to determine the smallest possible concentration that would improve oxidation stability to the level of six hours.

Based on the results obtained here, the following can be concluded: To ensure biodiesel reaching the six-hour OSI limit in Rancimat tests, a minimum concentration level of 2,000 ppm of the BioSineox antioxidant is required in the process sample.

The increase of the six-hour requirement to a minimum of eight hours in the standard 14214 necessitates further research in order to find the optimum concentration of the antioxidant. Most probably, the concentration needs to be higher than 2,000 ppm.

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# Using steam explosion pretreatment method for bioethanol production from floodplain meadow hay

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**Abstract.** This article investigates influence of the steam explosion pretreatment method at different temperatures on sugar conversion rates and bioethanol production efficiencies from floodplain meadow hay. Floodplain meadow hay is used as a raw material, because these semi-natural grasslands need regular maintenance to preserve their high biodiversity. So far, this biomass has been largely unused, but it could provide a good feedstock for bioethanol production.

In this work, steam explosion pretreatment is used in combination with enzymatic hydrolysis. Effects of steam explosion pretreatment on the fibre content and cell wall structure are also studied. Results from fibre analysis show, that the floodplain meadow hay has very high lignin content of 24.16%, but relatively low cellulose content of 27.19%. Highest cellulose to glucose conversion rate of 234.6 g kg$^{-1}$ and ethanol yield of 115.7 g kg$^{-1}$ of biomass were achieved with the steam explosion pretreatment at 200°C. Scanning electron microscope (SEM) images show that pretreatment at 150°C does very little damage to plant cells, while steam explosion at 200°C disintegrates most of the plant cell walls and exposes cellulose fibres.

**Key words:** floodplain meadow hay, glucose, bioethanol, steam explosion.

## INTRODUCTION

Biofuels are considered one of the most sustainable options in the foreseeable future for replacing fossil fuels in transportation sector (Nigam & Singh, 2011). The most widely produced biofuel in the world is bioethanol (Global Renewable Fuels Alliance, 2011). Most of the bioethanol is produced from corn or sugar cane, but the share of cellulosic bioethanol is rapidly increasing. The advantage of the cellulosic bioethanol, compared to traditional grain/sugar ethanol, is the fact that it is possible to use entire above-ground biomass of a plant for bioethanol production, thus enabling better efficiency and land use. Downside of the cellulosic bioethanol production is the need for large investments and sophisticated processing equipment (Stevens et al., 2004). In the future, the production of bioethanol is expected to include both, traditional grain/sugar crops and lignocellulosic materials (Demirbas, 2011).

Lignocellulosic raw materials represent the most abundant global resource for production of liquid biofuels (Lin & Tanaka, 2006; Talebnia et al., 2010). Since demand for biofuels has been increasing together with demand for food, a lot of

attention has been recently directed to the utilization of biomass from grasslands (McKendry, 2002; Heinsoo et al., 2010).

In Estonia, there is nearly 20,000 hectares of floodplain meadows with high biodiversity, that need regular maintenance (Kukk & Sammul, 2006). If these meadows are not maintained, they will quickly overgrow and lose much of their biodiversity. Floodplain meadows produce every year over 100,000 tons of biomass, which until now has found little use. In order to promote the management of semi-natural meadows, alternative uses for the biomass are required without changing the traditional management principals like harvesting time, avoidance of fertilizers and use of heavy equipment (Heinsoo et al., 2010). One alternative possibility is to use natural meadow hay as feedstock for bioethanol production and utilize it as a substitute for petrol. This would also help to promote rural development, reduce greenhouse gases and decrease the dependence from energy import (Demirbas, 2005).

Several different pretreatment methods for lignocellulosic biomass have been studied in the past. Among those, steam explosion and dilute acid pretreatment are the most widely used. In steam explosion pretreatment, lignocellulosic biomass is heated at elevated temperatures of 150–250°C with high pressure steam. After a few minutes of incubation time, the heated biomass is subjected to explosive decompression thereby, physically and chemically modifying the biomass (Cantarella et al., 2004). When biomass is exposed to high temperatures: hemicellulose is degraded, part of lignin is solubilized and cellulose binding is reduced. Under instantaneous decompression, superheated water flashes into steam and steam volume expands explosively. The impact force generated by flashing and volume expansion destroys cell structure. This tears materials into small pieces, cellulose fibre-bundles are separated from one another and their structures loosened thereby, re-distributing lignin and fully exposing cellulose (Chen & Zhang, 2012).

Dilute acid pretreatment uses cheap chemicals, mild operating conditions and is simple to perform. Downside of the dilute acid pretreatment method is a low conversion rate and formation of by-products that are inhibitory for the following fermentation process (Tutt et al., 2012; Tutt et al., 2013). Furthermore, most of the lignin remains intact. In the pretreatment with dilute acid, 0.5–1.5% sulphuric acid solution is added to the biomass to hydrolyse hemicellulose during 5–60 minutes at 130–200ºC. Higher temperatures require shorter time of pretreatment (Yang et al., 2009; Kim et al., 2011).

Aim of this research was to investigate bioethanol production from floodplain meadow hay and to compare at different conditions the influence of steam explosion pretreatment to the glucose and ethanol yield. Results from steam explosion pretreatment were also compared to the results of dilute acid pretreatment of floodplain meadow hay

## MATERIALS AND METHODS

### Biomass

Meadow hay samples were harvested in July, 2012, from the floodplains of Emajõgi. Samples were milled to a particle size of 1–3 mm and stored at a room temperature. Dry matter content of samples was 90.4%.

### Pretreatment

Steam explosion pretreatment was used in this work. Sample size was 900 g of pre-dried and milled hay, which was soaked in 900 g of distilled water. Pretreatment was performed in a laboratory scale steam explosion system, seen in Fig. 1, at the University of Applied Sciences Upper–Austria. Steam explosion was carried out at temperatures T = 150–200°C and incubation times of 10–30 minutes. Pretreated material was then dried at temperature T = 40°C to a dry matter content of 95%.
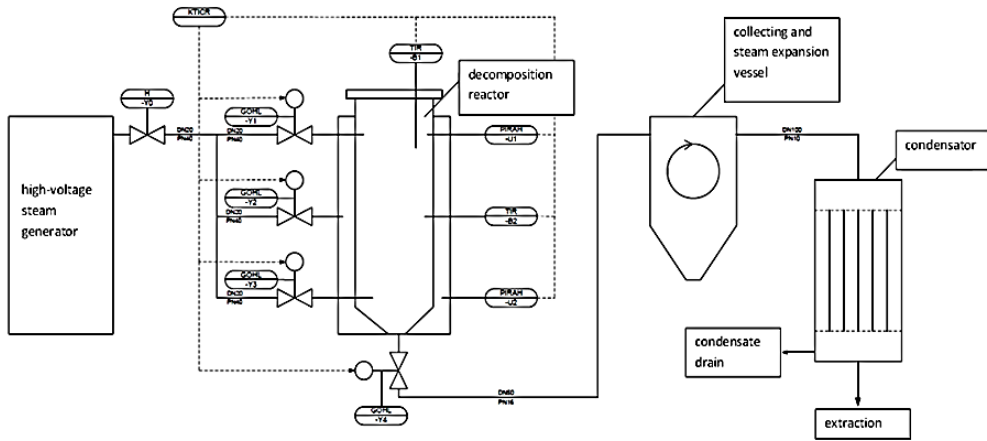


**Figure 1.** Laboratory scale steam explosion unit (Eisenhuber et al., 2013).

Pretreatment with dilute acid, followed by enzymatic hydrolysis, was used for the comparison tests. Size of the samples was 100 g of dried (DM 90.4%) and milled meadow hay to which 1,000 mL of 1% sulphuric acid solution was added. All samples were heated for t = 60 minutes at a temperature T = 130 ± 3°C and a pressure of p = 3 bar (Tutt et al., 2012; Tutt et al., 2013).

### Hydrolysis and fermentation

Pretreatment phase was followed by enzymatic hydrolysis with enzyme complex Accellerase 1500. Enzyme mixture was added to the sample at a ratio of 0.3 mL per g of biomass. Hydrolysis of the pretreated material was carried out at 10% dry matter content in citrate buffer, c = 50 mmol L$^{-1}$ and at pH = 5 (adjusted with NaOH). The samples were incubated for 72 h at 50°C in a shaking incubator at rotational speed of 2.5 s$^{-1}$.

Fermentation of glucose into ethanol was executed using yeast *Saccharomyces cerevisiae* in 1 litre bottles that were sealed with fermentation tubes. Volume of fermentation medium was 500 mL. Fermentation medium had a pH = 4.6 which was adjusted with H$_2$SO$_4$. Fermentation medium contained 100 mL hydrolysate, 2 mL CaCl$_2$·2H$_2$O, 2 mL KH$_2$PO$_4$, 2 mL MgSO$_4$·7H$_2$O, 0.44 g (NH$_4$)$_2$HPO$_4$. Yeast suspension (2 mL) was added to the solution and fermentation was carried out at 30°C for 120 hours.

**Analysis**

Dry matter content was analysed with a moisture analyser Ohaus MB 45. The fibre analysis (cellulose, hemicellulose and lignin) was performed according to the methods of Association of Official Analytical Chemists (AOAC 973.18) and methods by Tecator company (fibre determination using Tecator, Part No. 1000 1217, Serial No. 1706, U = 200 - 240 V, f = 50/60 Hz, P = 1,000 W). Fibre analysis results were also checked with acid hydrolysis. Acid hydrolysis was done according to the methods of National Renewable Energy Laboratory of USA for determination of structural carbohydrates and lignin in biomass (NREL, 2012).

Saccharides, organic acids, ethanol and furans in sample solutions were measured by high performance liquid chromatography (HPLC). The HPLC system Agilent Technologies 1200 Series with a Varian Metacarb 87 H column (300·7.8 mm) at 65°C, $H_2SO_4$ (c = 5 mmol $L^{-1}$) eluent and an isocratic flow rate of 0.8 mL $min^{-1}$ was used. The signals were acquired with a refractive index (RI) and a UV–detector at 210 nm wavelength.

In order to compare the morphological structure of untreated and steam exploded raw material, scanning electron microscope (SEM) images were taken with a scanning electron microscope VEGA 2 LMU from Tescan.

Averaged results are used in figures and standard deviations are shown by vertical lines. Data was processed with programs Microsoft Excel and GraphPad Prism 5.

## RESULTS AND DISCUSSION

Bioethanol production from natural meadow hay using steam explosion pretreatment was studied in this work. Glucose and ethanol results were compared with those from dilute acid pretreatment method that had been used previously for meadow hay pretreatment.

**Table 1.** Cellulose, hemicellulose, lignin and dry matter content of meadow hay samples (HS150– steam exploded hay at 150°C)

| | Cellulose (%) | $STD_2$ (%) | Hemicellulose (%) | $STD_2$ (%) | Lignin (%) | $STD_2$ (%) | Dry matter (%) |
|---|---|---|---|---|---|---|---|
| Hay (untreated) | 27.19 | 0.69 | 29.15 | 0.48 | 24.16 | 0.29 | 90.43 |
| HS150 | 32.66 | 0.23 | 26.51 | 0.15 | 26.49 | 0.31 | 93.46 |
| HS170 | 33.42 | 1.11 | 25.98 | 0.38 | 28.82 | 0.12 | 93.96 |
| HS180 | 33.87 | 0.36 | 24.63 | 1.02 | 29.05 | 0.09 | 95.20 |
| HS200 | 35.07 | 0.36 | 15.27 | 0.48 | 33.71 | 0.17 | 95.83 |

Results from fibre analysis show that natural meadow hay, which was cut in the middle of July, has fully matured and therefore, has very high lignin content of 24.16%, but relatively low cellulose content of 27.19% in the untreated sample, see Table 1. Meadow hay also has relatively high hemicellulose content of 29.15%, which makes it difficult for enzyme molecules to reach cellulose fibres and degrade these into glucose without using adequate pretreatment conditions. High content of lignin in plant fibres leads to a creation of protective barrier that prevents plant cell destruction by

fungi and bacteria. For the conversion of biomass to biofuel, the cellulose and hemicellulose must be broken down into their corresponding monomers (Kumar et al., 2009).

Steam explosion pretreatment disrupts the structure of plant cell walls and removes hemicellulose, but it dissolves only a fraction of lignin. Approximately 95% of lignin remains in an insoluble form. Since no chemicals are used in the pretreatment phase, the steam explosion method requires high temperatures to effectively dissolve hemicellulose, as seen in Fig. 2. Effectiveness of steam explosion increases rapidly at temperatures over 180°C. Steam explosion at 200°C lowers hemicellulose content of meadow hay sample to 15.27%, compared to the 29.15% in the untreated sample.
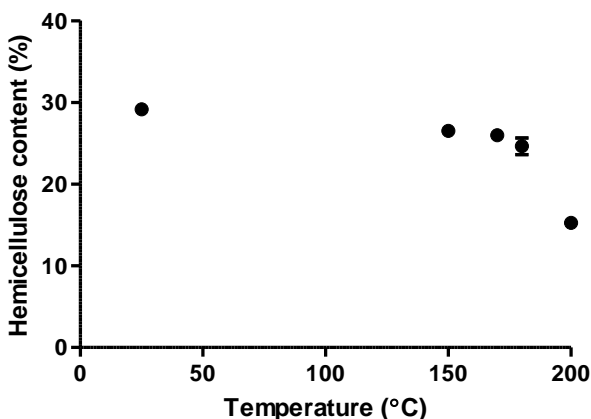


**Figure 2.** The correlation of hemicellulose content in meadow hay samples, from steam explosion pretreatment temperatures.

Scanning electron microscope images also confirm that steam explosion at 200°C is very effective in disrupting the plant cell wall structure, while temperatures under 180°C clearly seem to be inadequate, see Fig. 3. SEM images show that steam explosion at 150°C has done very little damage to cell walls compared to the untreated sample, while steam explosion at 200°C has destroyed most of the cell walls and exposed cellulose fibres.

Hydrolysis results show that the highest cellulose to glucose conversion rate of 234.6 g kg^{-1} of biomass was achieved with the steam explosion pretreatment at 200°C (results shown in Fig. 4). This shows that steam explosion at 200°C removes most of the hemicellulose from the sample and leaves the cellulose fibres easily accessible for enzymes. By far the lowest glucose yield of 83.8 g kg^{-1} was achieved by steam explosion pretreatment at 150°C. Although the pretreatment temperature was only 50 degrees lower, the glucose yield was 2.8 times smaller than the results achieved with pretreatment at 200°C temperatures. This shows that steam explosion conditions at 150°C are not effective enough to remove hemicellulose from the samples.
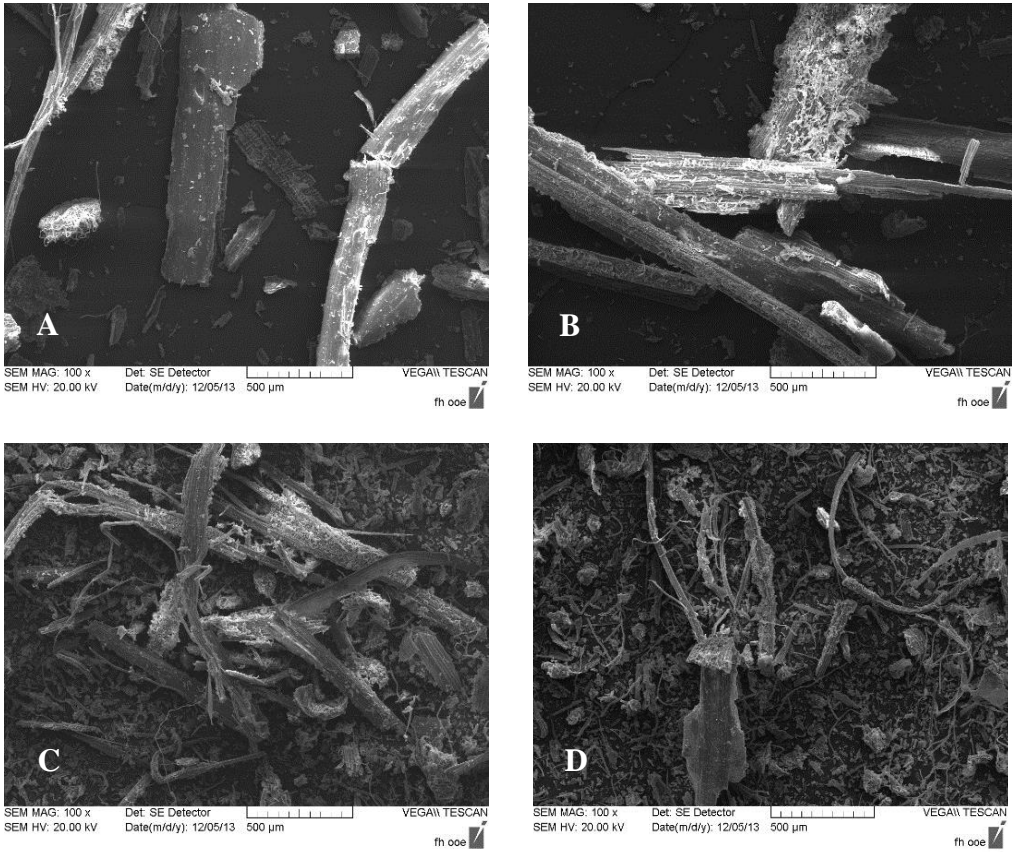
**Figure 3.** Comparison of scanning electron microscope (SEM) images of meadow hay samples – untreated (A) and steam exploded at different temperatures (B – 150°C, C – 170°C, and D – 200°C).
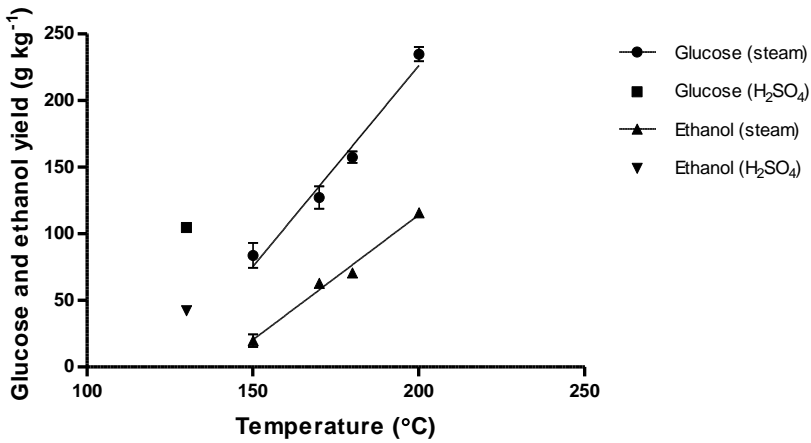


**Figure 4.** Influence of different pretreatment conditions on the glucose and ethanol yields from floodplain meadow hay samples.

The same correlation was also seen between steam explosion temperature and ethanol yield. The highest ethanol yield of 115.7 g kg$^{-1}$ was achieved by pretreatment at 200°C and the lowest ethanol yield of 19.8 g kg$^{-1}$ was achieved by pretreatment at 150°C.

**Table 2.** Hydrolysis and fermentation efficiencies at different pretreatment conditions (HS- steam explosion pretreatment at temperatures 150–200°C; HD- dilute acid pretreatment at 130°C)

| Pretreatment method | Glucose yield g kg$^{-1}$ | Ethanol yield g kg$^{-1}$ | Hydrolysis efficiency % | Fermentation efficiency % |
|---|---|---|---|---|
| HS150 | 83.8 | 19.8 | 30.8 | 46.2 |
| HS170 | 127.1 | 62.8 | 46.7 | 96.9 |
| HS180 | 157.4 | 70.7 | 57.9 | 88.1 |
| HS200 | 234.6 | 115.7 | 86.3 | 96.7 |
| HD130 | 115.2 | 41.1 | 42.4 | 69.8 |

The floodplain meadow hay pretreated with dilute acid gave glucose and ethanol yields of 115.2 g kg$^{-1}$ and 41.1 g kg$^{-1}$, respectively. This shows that pretreatment of meadow hay with dilute acid is more effective than steam explosion at 150°C, but less effective than steam explosion pretreatment at temperatures over 170°C. Hydrolysis efficiencies at different pretreatment conditions are given in Table 2. The highest hydrolysis efficiency of 86.3% and one of the highest fermentation efficiencies of 96.7% was achieved by steam explosion at 200°C.

## CONCLUSIONS

Results from fibre analysis show, that natural meadow hay has very high lignin content of 24.16%, but relatively low cellulose content of 27.19%. This means that it is difficult for enzyme molecules to reach cellulose fibres and degrade these into glucose without using high temperature pretreatment conditions.

Highest cellulose to glucose conversion rate of 234.6 g kg$^{-1}$ and ethanol yield of 115.7 g kg$^{-1}$ of biomass were achieved with the steam explosion pretreatment at 200°C. The lowest glucose yield of 83.6 g kg$^{-1}$ and ethanol yield of 19.8 g kg$^{-1}$ were given by samples pretreated with steam explosion at 150°C. These results were confirmed by scanning electron microscope images which show that pretreatment at 150°C does very little damage to plant cell walls. Fully matured meadow hay is quite durable to steam explosion pretreatment thus, higher temperatures and harsher conditions, preferably 200°C have to be used.

Although floodplain meadow hay has relatively low cellulose content and high lignin content, it is suitable raw material for bioethanol production. Floodplain meadows produce over 100,000 tons of biomass per year and if steam explosion pretreatment at 200°C, followed by enzymatic hydrolysis, is used, then it would be possible to produce approximately 11,570 tons of bioethanol from this biomass.

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# The effect of biofuels on the quality and purity of engine oil

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**Abstract.** The European Union aims to promote the use of biofuels and thus set a commitment to the expansion of biofuels in transport. Biofuels replace fossil fuels mainly in part, the creation of biodiesel. For gasoline engines, the most widely used biofuel is E85, a fuel containing 85% ethanol and 15% gasoline. The more bio-components are contained in a fuel, the more oil filling the combustion engine suffers. Therefore, in this paper, a comparison of the properties of oil filling when using fossil fuels (currently contains a small amount of the fuel ethanol) and the E85 biofuel is provided. The cars Saab 95 and 93 are monitored, namely the motors B235 R, B207 L, and B205 L. For each car, the total of 10 samples of engine oil were taken. One part of the samples was collected during operation of the internal combustion engine on the biofuel E85 and the second during operation of the internal combustion engine on the fossil fuel BA95. Both vehicles used the same engine oil, Mobil 1 0W-40, for lubrication of the internal combustion engine. The analyses of the engine oil are focused on the evaluation of the kinematic viscosity and density at 40 and 100°C.

**Key words:** biofuel, oil, viscosity.

## INTRODUCTION

In recent years, the European Union has devoted increasing attention to the possibility of using biofuels as a source of energy for transportation. The main requirements for bio include the requirement for similar chemical and physical properties to conventional fuel.

The E85 fuel is currently promoted as the most widely used substitute to fossil fuels, which cover most of the energy consumption in the transport sector, particularly in the automotive industry.

E85 is a fuel mixture, which contains 85% ethanol and 15% BA95. The composition of ethanol may vary depending on the season. The E85 fuel is exempted from excise duty in the Czech Republic (AUTO INZAT, 2014).

The standard ethanol component of E85 can be made of any crop which contains carbohydrates, i.e. grass over potatoes, cereals to beet. The raw material can be any lignocelluloses-containing biomass such as wood, sawdust or waste in the manufacture of pulp and paper (AUTO INZAT, 2014).

The aim of this paper is to compare the influence of fossil fuel and the biofuel E85 on the quality and cleanliness of engine oil. Measurements were carried out on the private car brand Saab 95 and 93, namely the motors B235 R, L and R B205, L. For each car, the total of 10 oil samples were taken. One part of the ethanol samples was from a driven vehicle and the other from a motor operated on fossil fuel.

The analysis of the motor oil is focused on the viscosity, which is a measure of the flow ability of liquids. Oils with lower viscosity are more fluid (less dense) and have a smaller internal flow resistance against the flow. Higher oil viscosity (thicker oil) turn means higher resistance and thus a slower rate, figuratively, and higher resistance to movement between two lubricated parts. The viscosity of motor oil is very important and is probably the best-known property of oil (Černý, 2006).

The viscosity (or the rate of internal friction ) of lubricating oil is not a constant value, but depends on the environmental conditions. During engine operation, there are changes in temperature and pressure and it is desirable that the viscosity of the oil under these conditions changes as little as possible. The dependence of oil viscosity on temperature is expressed by the so-called viscosity index (VI). The higher the VI, the less the viscosity changes with temperature changes in the engine. The viscosity index is given in the catalogues of the manufacturers of automotive lubricants. For common designation, the viscosity properties of engine oil are used exclusively in the classification of the SAE (Society of Automotive Engineers, USA). This standard is used for classifying oils into 6 winter classes marked with a number and the letter 'W' (from the English word "Winter") and 5 summer classes with designated numbers. The number is dimensionless and does not relate to any physical quantity. Nevertheless, it is an analogy to viscosity. Thus, if the value is higher, the oil is viscous at the designated temperature (Černý, 2006). The viscosity index is a value calculated from the kinematic viscosity, usually at 40°C and 100°C (Anton Paar, 2014). In Fig. 1, there is an example of viscosity and temperature.
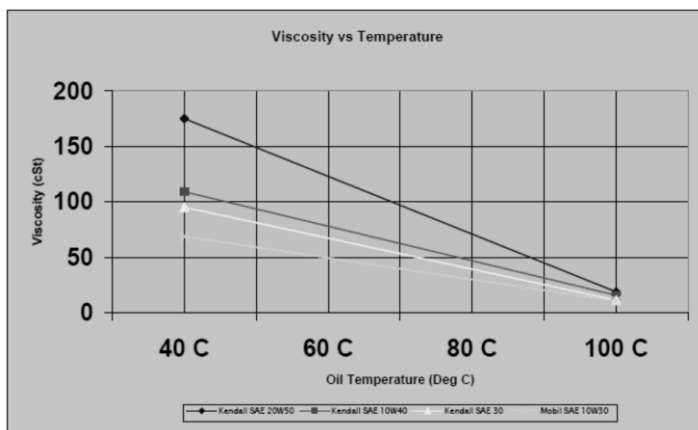


**Figure 1.** Dependence between viscosity and temperature (Toepfer, 2014).

The classification of the oils by the viscosity classes of the SAE and ISO-VG is performed by measuring the viscosity in new, unused oil. However, several tens of hours of operation may change the viscosity of oil. The viscosity of oil can reduce with intense mixing or increase by the force of oxidation. The change in the viscosity may be so significant that the oil classifies into a different viscosity class of the SAE or ISO-VG. This can have a very negative impact on the durability of the device, which is lubricated with the oil (Toepfer, 2014).

## MATERIALS AND METHODS

The oils of the abovementioned combustion engines were analysed using a Stabinger viscometer. The viscometer SVM 3000 Stabinger is a modified rotary viscometer, which is used for measuring the viscosity and density of oils and liquid fuels in accordance with ASTM D7042. From the measured values of dynamic viscosity (mPa·s) and liquid density (kg m$^{-3}$), the unit automatically calculates the kinematic viscosity (mm$^2$ s$^{-1}$) and viscosity index according to ASTM D 2270/ISO 2909 (Sejkorová, 2013).

The principle for determining the dynamic viscosity is determination of the stable rotational speed for measuring of the rotor with an integral magnet that floats in the sample, which is a filled tube rotating at a constant speed. The stable measuring speed of the rotor is achieved when the braking effects of the eddy electric field and shear stress generated in the sample are balanced. The small volume of sample required for the analysis allows extremely rapid temperature changes and a very short time to reach the equilibrium (Sejkorová, 2013). An example of a Stabinger viscometer is provided in Fig. 2.



**Figure 2.** Stabinger viscometer (IRTEK, 2008).

Measurement of the viscosity is based on measurement of torsion and viscosity. The rotating magnet in 3000 SVM generates an eddy electric field with the exact dependence brake torsion. The swirl braking field is measured with high accuracy. In combination with an integrated thermoelectric thermostat, this provides extremely accurate results. The resolution when measuring the voltage is only 50 pico Nm. Therefore, it only requires a very compact measuring cell (Anton Paar, 2014).

The accuracy obtained by the SVM 3000 in the laboratory study of the ASTM subcommittee D02.07A has been shown to be equivalent to the accuracy achieved in the measurements made according to the ASTM D445. No significant bias can be found between the methods. The extremely high sensitivity of the eddy current torque measuring thermoelectric temperature control system provides unparalleled precision. The resolution moment is unmatched: 50 pico – Nm. This is comparable with the torque resulting from dust particles to 1 cm lever arm and allows minimization of the measuring cell (IRTEK, 2008).

In the observed passenger car brand Saab, engine oil with Mobil 1 0W-40 designation was used. Table 1 shows the specific parameters of the new engine oil from the safety data sheet of the indicated manufacturer.

Table 1. Parameters analysed for the new Mobil 1 0W-40

| Oil – Mobil 1 0W40 | 40°C | 100°C |
|---|---|---|
| Viscosity ($mm^2 s^{-1}$) | 71.0 | 13.5 |
| Density ($g cm^{-3}$) | 0.865 | Unknown |

## RESULTS

First, we analysed the viscosity and density of pure oil Mobil 1 0W40 to determine whether the data provided in the manufacturer's safety data sheet corresponded to reality. For the measured values, see Table 2. The measurements for statistical control were performed 10 times and Table 2 shows the average of these values.

Table 2. Average of net oil Mobil 1 0W-40

| Oil – Mobil 1 0W40 | 40°C | 100°C |
|---|---|---|
| Viscosity ($mm^2 s^{-1}$) | 75.127 | 13.516 |
| Density ($g cm^{-3}$) | 0.833 | 0.795 |

The viscosity of pure oil at 40°C was measured 4.127 $mm^2 s^{-1}$ higher than the value given in the safety data sheet of the manufacturer. The density at 40°C of the pure sample was 0.032 $g cm^{-3}$ lower. These differences between the safety data sheet and the analysis of pure oils are negligible and it can be said that the analysed pure oil at 40°C corresponds to reality. When measuring the viscosity at the temperature of 100°C, the values were almost equal, the difference was about 0.016 higher for pure oil; again, the values correspond to the reality.

Furthermore, for measuring the viscosity of the engine oil of the first automobile 95 with an engine Saab Turbo 2.3, with performance 184 kW, engine identification B235 R and vintage 2004, the samples were taken after 7,000 km. The data of the viscosity and density at measured temperatures 40 to 100°C are presented in Table 3.

Table 3. Viscosity and density at 40 and 100°C in the car Saab 95

| | Saab 95 | |
|---|---|---|
| | Fuel E85 | Fuel BA95 |
| Viscosity at 40°C | 69.379 $mm^2 s^{-1}$ | 70.993 $mm^2 s^{-1}$ |
| Viscosity at 100°C | unmeasurable | 13.010 $mm^2 s^{-1}$ |
| Density at 40°C | 0.698 $g cm^{-3}$ | 0.853 $g cm^{-3}$ |
| Density at 100°C | unmeasurable | 0.814 $g cm^{-3}$ |

The measured values show that the viscosity and density of the engine oil when using E85 decreased by up to 20%. The measured kinematic viscosity at 40°C was about 5.748 $mm^2 s^{-1}$ lower than that of pure oil. The density was about 0.135 $g cm^{-3}$ lower compared to pure oil. It was not possible to measure the viscosity and density at 100°C, since the device's value could not be recorded.

Regarding the use of the fossil fuel BA95, the viscosity and density at both the engine oil temperature of 40°C and for the temperature of 100°C deviate within the maximum of percent units, i.e. it can be stated that it corresponds to pure oil.

The second type of car was the Saab 93 with the engine volume 2.0 Turbo, performance 129 kW, engine identification B207 L, and vintage 2003, where the samples were taken after 7,000 km. The data of the viscosity and density measured at the temperatures 40 to 100°C are given in Table 4 below.

**Table 4.** Viscosity and density at 40 and 100°C in the car Saab 93

| | Saab 93 | |
| --- | --- | --- |
| | Fuel E85 | Fuel BA95 |
| Viscosity at 40°C | 69.263 mm$^2$ s$^{-1}$ | 70.561 mm$^2$ s$^{-1}$ |
| Viscosity at 100°C | unmeasurable | 12.986 mm$^2$ s$^{-1}$ |
| Density at 40°C | 0.648 g cm$^{-3}$ | 0.842 g cm$^{-3}$ |
| Density at 100°C | unmeasurable | 0.786 g cm$^{-3}$ |

From the measured values, it again appears that the viscosity and density of the engine oil decreased by more than 20% when using E85. The viscosity measured at 40°C was about 5.864 mm$^2$ s$^{-1}$ lower than that of pure oil. The density was 0.185 g cm$^{-3}$ lower than that of pure oil. It was again not possible to measure the viscosity and density at 100° C.

Regarding the use of the fossil fuel BA95, the viscosity and density at both the engine oil temperature of 40°C and for the temperature of 100°C deviate within the maximum of percent units, i.e., again, it can be noted that the values correspond to clear oil.

The third type of car was the Saab 95 with the volume of engine 2.0 Turbo, performance 110 kW, engine identification B205 L and vintage 2002, where the samples were taken after 7,000 km. The data of the viscosity and density of the vehicle were measured at measured the temperatures 40 to 100°C and are shown in Table 5.

**Table 5.** Viscosity and density at 40 and 100°C in the car Saab 95

| | Saab 95 | |
| --- | --- | --- |
| | Fuel E85 | Fuel BA95 |
| Viscosity at 40°C | 68.873 mm$^2$ s$^{-1}$ | 70.243 mm$^2$ s$^{-1}$ |
| Viscosity at 100°C | unmeasurable | 12.763 mm$^2$ s$^{-1}$ |
| Density at 40°C | 0.624 g cm$^{-3}$ | 0.824 g cm$^{-3}$ |
| Density at 100°C | unmeasurable | 0.782 g cm$^{-3}$ |

From the measured values, it again appears that the viscosity and density of the engine oil decreased by more than 20% when using E85. The viscosity at 40°C was about 6.254 mm$^2$ s$^{-1}$ lower than that of pure oil. The density was about 0.209 g cm$^{-3}$ lower compared to pure oil. It was again not possible to measure the viscosity and density at 100°C.

The engine oil when using fossil fuel BA95 has the viscosity and density at both the temperature of 40°C and the temperature of 100°C with the deviation of an acceptable percentage, thus, again, it can be noted that the values correspond to clear oil.

## CONCLUSIONS

We used the Viscometer SVM 3000 Stabinger with which the kinematic viscosity and density of the engine oil were measured. These two values were measured at temperatures from 40 to 100°C. The measured values were compared with those of clean engine oil Mobil 1 0W-40, which had the same characteristics with the manufacturer's safety data sheet for that type of motor oil.

The analysis of engine oil was carried out on three types of cars of the brands Saab, which ran on two different fuels. The sampling interval of the oils was about 7,000 km. The measured results are shown in Tables 2, 3, 4 and 5.

From the measured values, it is clear that using E85 decreases the viscosity and density of the engine oil at 40 and at 100°C for all three cars and by more than 20%. When using a fuel with 95 octane values, the difference in the viscosity and density compared to pure engine oil in hundredths of a percent can be considered satisfactory. However, a change of more than 20% is regarded as critical in order to change the engine oil.

The lower viscosity and density when running on the E85 fuel reduce the lubricity of the engine oil and cause the risk of damage to engine components. To prevent or at least limit this, it is necessary to operate the engine running on E85 with a significantly shorter replacement interval, and it must also be halved.

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