Lignocellulosic Biobutanol as Fuel for Diesel Engines

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Energy recovery of lignocellulosic waste material in the form of liquid fractions can yield alcohol-based fuels such as bioethanol or biobutanol. This study examined biobutanol derived from lignocellulosic material that was then used as an additive for diesel engines. Biobutanol was used in fuel mixtures with fatty acid methyl ester (FAME) obtained by esterification of animal fat (also a waste material) in the amounts of 10%, 30%, and 50% butanol. 100% diesel and 100% FAME were used as reference fuels. The evaluation concerned the fuel's effect on the external speed characteristics, harmful exhaust emissions, and fuel consumption while using the Non-Road Steady Cycle test. When the percentage of butanol was increased, the torque and the power decreased and the brake specific fuel consumption increased. The main advantage of using biobutanol in fuel was its positive effect on reducing the fuel's viscosity.

Keywords: Biofuel; Lignocellulosic biobutanol; Harmful emissions; Performance parameters; Engine

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INTRODUCTION

One of the many ways to utilize the wood waste is for energy purposes (Chen *et al.* 2016; Guo *et al.* 2015), *e.g.*, for the production of gaseous (Biagini *et al.* 2015) or liquid biofuels such as biodiesel (Chen *et al.* 2016), bioethanol (Shadbahr *et al.* 2015), or biobutanol (Jurgens *et al.* 2012).

The production of alcohol-based biofuels from lignocellulose is a promising alternative to traditional biofuel production that uses food ingredients (first-generation biofuels) (Desai et al. 2014). The most commonly used alcohol-based fuel is ethanol. However, ethanol is not widely used as a fuel for diesel engines because of its low cetane number, decreased flash point, low lubricity, low energy content, poor miscibility, and high volatility (Kleinová et al. 2011). Butanol can serve as a favorable alternative to ethanol because it has a lower auto-ignition temperature, is less evaporative, and releases more energy per unit of mass. It also has a higher cetane number, higher energy content, and better lubricating ability than both ethanol and methanol (Hönig et al. 2014; Mařík et al. 2014). Butanol is less corrosive and has better miscibility with vegetable oils, diesel, and fatty acid methyl ester (FAME). The mixture of butanol and FAME, or butanol and diesel, slightly increases the brake specific fuel consumption. It also lowers the temperature of the exhaust gases because its heating value is lower than diesel (Bhattacharya et al. 2003; Doğan 2011; Yilmaz et al. 2014). Another advantage of butanol is its ability to reduce the viscosity of composite fuels, particularly when it is mixed with FAME or crude vegetable oil (Čedík et al. 2015).

Producing butanol by means of biochemistry uses different kinds of bacteria, commonly those involving *Clostridium acetobutylicum* (Raganati *et al.* 2014; Procentese *et al.* 2015; Raganati *et al.* 2015). Producing butanol thermochemically from lignocellulosic materials may be another promising possibility (Okoli and Adams 2014, 2015). In order to make possible the commercialization of the fuel, the most important in biobutanol production process is to improve efficiency and profitability of the acetone-butanol-ethanol fermentation process and utilization of waste material as a feedstock (Ranjan and Moholkar 2012, Ranjan *et al.* 2013).

In the case of the diesel engines, the most common alternative to fossil fuels is FAME. It has lower calorific value, higher density, and higher viscosity in comparison with diesel (Pexa and Mařík 2014). FAME can be produced from vegetable or animal fat (Sirviö *et. al.* 2014). The main disadvantages of FAME include inferior storage and oxidative stability, as well as high feedstock cost, particularly when using vegetable oil as a raw material. This disadvantage can be overcome by using animal fat, which is currently considered a waste product (Barrios *et al.* 2014; Čedík *et al.* 2015).

The aim of this study was to determine the effect of the animal fat-based mixture of butanol and FAME on brake specific fuel consumption and specific emissions (carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO), hydrocarbons (HC), flowmeter, and PM (Particulate Matter) in g/kWh) of the supercharged diesel engine. Emissions of PM are composed of primary carbon, organic carbon, and small amount of sulfate, nitrogen and water. The proportion of basic carbon is approx. 75 % (Hromádko *et al.* 2011).

The Non-Road Steady Cycle (NRSC) was used for the assessment (ISO 8178-4 2007, European Parliament and the Council of the European Union 1997, 2000, 2004, 2005).

EXPERIMENTAL

Materials

The tractor Zetor 8641 Forterra (Brno, Czech Republic), production number 1204, was used to test the composite fuels with biobutanol. Its engine is a supercharged four-cylinder diesel engine. Prior to testing, it had worked for 100 h. The measurement diagram is presented in Fig. 1.

The dynamometer AW NEB 400 (Pontiac, United States) (Fig. 1b) was connected to the output shaft of the combustion engine (Fig. 1k). The engine parameters are presented in Table 1, and the dynamometer parameters are presented in Table 2. The fuel consumption was measured by means of the scale VIBRA 6200 J (Tokyo, Japan) (Fig. 1f) with a measuring range from 0 to 6200 g and an accuracy of 0.1 g. Fuel gauges (Figs. 1h and 1i) with thermometers had a control function. Gaseous components of emissions were recorded by means of the device BrainBee AGS 200 (Parma, Italy) (Fig. 1c). Solid components of emissions were recorded by means of the device BrainBee OPA 100 (Parma, Italy) (Fig. 1d). The accuracy and range of measurement of the device BrainBee are presented in Table 3. To convert emissions values to the weight unit, the amount of intake air was measured by means of a wireless nozzle (Fig. 1e). All measured quantities were transferred by means of the A/D converter LabJack U6 (Lakewood, United States) and the module for pulse sensors Papouch Quido 10/1 (Prague, Czech Republic) (Fig. 1a) to the superior measuring computer HP Mini 5103 (Houston, United States).

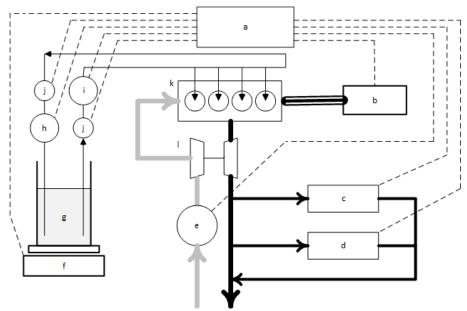


Fig. 1. Measurement diagram: a) datalogger + PC, b) dynamometer, c) Analyzer of gaseous components of emissions, d) opacimeter, e) measuring the amount of intake air, f) weight, g) external tank, h) fuel gauge (return to engine), i) fuel gauge (intake), j) thermometer, k) engine, l) blower

Table 1. Basic Technical Parameters of the Tractor Zetor Forterra 8641 (According to the Producer)

Parameter	Value
Rated engine power according to ECE 24 (kW)	60
Rated speed (1/min)	2200
Maximum torque (Nm)	351
Specific consumption at rated power (g/kWh)	253

Table 2. Basic Technical Parameters of the Dynamometer AW NEB 400

Parameter	Value
Maximum torque on PTO (Nm)	2850
Maximum breaking performance (kW)	343
Measurement error (%)	2

 Table 3. Parameters of the Emission Analyzer BrainBee

Component	Resolution	Accuracy				
CO	0.01 % vol.	0.03 % vol. or 5 % read value				
CO ₂	0.1 % vol.	0.5 % vol. or 5 % read value				
HC	1 ppm vol.	10 ppm vol. or 5 % read value				
O ₂	0.01 % vol.	0.1 % vol. or 5 % read value				
NO	1 ppm	10 ppm vol. or 5 % read value				
Opacity	0.1 %	2 %				
Temperature	1 °C	2.5 °C				

Density and viscosity of fuels in Fig. 3 were measured by means of the viscometer according to Stabinger SVM 3000 (Quebec, Canada). The accuracy of the viscometer was ± 0.5 kg·cm⁻³ for density and ± 0.35 % for viscosity.

Methods

Comparison of the selected mixed biofuels was performed according to the NRSC test in accordance with the standard ISO 8178-4 (type C1; 2007). The NRSC test helped to measure the engine mode in eight clearly defined points. Based on the external speed characteristics, the measuring points of the NRSC test were determined in accordance with the regulation 97/68/ES (European Parliament and the Council of the European Union 1997):

- **rated speed** means the maximum speed specified by the producer, which the regulator allows to reach at full load;
- **intermediate speed** means the engine speed, and it is the speed at maximum engine torque, if the speed ranges between 60 and 75% of the nominal speed;
- load means the percentage of the maximum available torque at the set speed;
- **weighting factor** means the weight of the set mode when calculating the final fuel consumption.

After determining the measuring points of the NRSC test, the fuel consumption and the emissions were measured at each point of the test. The brake specific fuel consumption and specific emissions (g/kWh) were calculated according to the relation within the whole test (Eq. 1),

$$m_{NRSC} = \frac{\sum_{i=1}^{8} \left(M_{P,i} \cdot VF_{i} \right)}{\sum_{i=1}^{8} \left(P_{PTO,i} \cdot VF_{i} \right)}$$

$$(1)$$

where m_{NRSC} is the specific consumption or specific emissions over the NRSC test (g/kWh), $M_{P,i}$ is the weight hourly fuel consumption or production of emissions in the i mode (g/h), VF_i is the weighting factor of the i mode (-), and $P_{PTO,i}$ is the engine power on PTO in the i mode (kW).

The tested mixed fuels are listed in the Table 4.

Table 4. Tested Fuels

Mixed biofuels	Share of fuels	Density at 15 °C (kg.m ⁻³)	Kinematic viskosity at 40 °C (mm².s ⁻¹)	Calorific value (MJ.kg ⁻¹)
Biobutanol/FAME (10_BUT)	(10%/90%)	869.9	3.88	37.69
Biobutanol/FAME (30_BUT)	(30%/70%)	855.7	3.04	36.67
Biobutanol/FAME (50_BUT)	(50%/50%)	844.5	2.68	35.65
FAME (100_FAME)	(100%)	886.4	4.32	38.2
Diesel – EN 590 (100_Diesel)	(100%)	836.9	2.68	42.6

FAME was produced from waste pork fat, which was melted and sterilised under high 0.3 MPa pressure and temperature above 130 °C during at least 20 min. This was

followed by drying until meat and bone mash appeared, from which extraction processes separated fat and animal powder. Pressure was decreased gradually to dry all moisture from the sample. The dried sample was warmed at 80 °C and put under 300 kg·cm⁻² pressure. Liquid fat appeared after releasing the pressure, but it became solid again at 40 to 50 °C. A higher acidity number differentiates fat obtained by this procedure from properties of homogeneous fats. Water was removed from fat and impurities in decanters. Methanol:fat 10:1 % wt. with 2 to 3 % wt. of sulphur acid was blended under a temperature of 90 to 95 °C for transesterification during 6 to 7 h to reach 90% of methyl esters. Esterification was performed by warming in balloons with feedback water cooler. Tested butanol (n-butanol) was in p.a. quality (LachNer, Ltd). Figure 2 shows a simplified diagram of the production process of biobutanol.

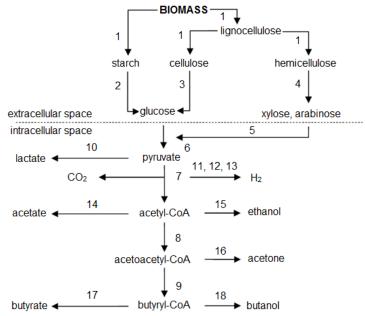


Fig. 2. Simplified conversion of plant biomass to solvents in bacteria of the genus *Clostridium* (Lipovský *et al.* 2009)

- 1. grain pretreatment/lignocellulose;
- 2. hydrolysis of starch (α -amylase, β -amylase, pullulanase, glucoamylase, α -glucosidase);
- 3. hydrolysis of cellulose (cellulase, β-glucosidase);
- 4. hydrolysis of hemicellulose;
- 5. absorption xylose/arabinose and subsequent transformation to fructose-6-phosphate and glyceraldehyde-3-phosphate
- 6. transmission of glucose and conversion to pyruvate;
- 7. pyruvate-ferredoxin oxidoreductase;
- 8. thiolase:
- 9. 3-hydroxybutyl-CoA (Coenzyme A) dehydrogenase, crotonase and butyryl-CoA dehydrogenase;
- 10. lactate dehydrogenase;
- 11. NADH (reduced nicotinamide adenine dinucleotide)-ferredoxin oxidoreductase;
- NADPH (reduced nicotinamide adenine dinucleotide phosphate)-ferredoxin oxidoreductase;
- 13. hydrogenase;
- 14. acetyltransferase phosphate, acetate kinase;
- 15. acetaldehyde dehydrogenase, ethanol dehydrogenase;
- 16. acetoacetyl-CoA: acetate/butyrate: CoA transferase, acetoacetate decarboxylase;
- 17. butyltransferase phosphate, butyrate kinase;
- 18. butyraldehyde dehydrogenase, butanol dehydrogenase.

RESULTS AND DISCUSSION

Figure 3 depicts the dependence of the kinematic viscosity at 40 °C and the density at 15 °C. These were two important parameters of the fuel that affected the wear of the fuel system. Figure 3 shows that biobutanol had a significant influence on the density and viscosity of the fuel. Higher mixing ratios of biobutanol can help to obtain fuel that meets the standards, *i.e.*, EN 14214 (2012) for methyl ester or EN 590 (2013) for diesel. These ratios were not problematic because of the good lubricating ability of biobutanol. The limit in the mixing ratio was set according to the cetane number of the mixture and the possibility of starting the combustion engine.

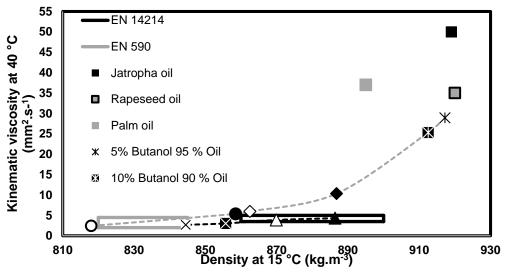


Fig. 3. Density and kinematic viscosity of biofuels

The decline of the performance parameters, of up to 20%, was expected because of the low cetane number and the heating value of biobutanol. Figure 4 shows this decline.

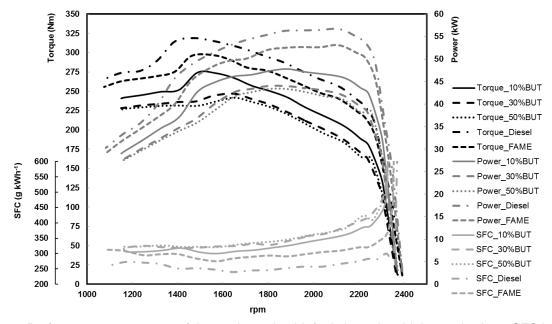


Fig. 4. Performance parameters of the engine using biofuels based on biobutanol, where SFC is the brake specific fuel consumption

Concerning the combustion engine performance, the torque reserve is also an important value. The values given in Table 5 make clear that the biobutanol fuel that contained FAME allowed preservation of the torque reserve's original value, or one better.

Table 5. Torque Reserve

Zetor 8641 Forterra	10_BUT	30_BUT	50_BUT	100_FAME	100_Diesel
Torque reserve (%)	43.9	42.6	44.6	34.8	40.7

The NRSC test was based on measuring eight points that were thus measured for the biobutanol-based fuel. They are presented in Table 6. The resulting values of the NRSC test are presented in Table 7. The values include brake specific fuel consumption, specific production of carbon dioxide, hydrocarbons, PM, and nitrogen oxide.

Results presented in Table 7 and Fig. 5 make clear that the biobutanol-based fuel contributed to a decrease in the production of nitrogen oxides and PM. In comparison with the diesel oil, nitrogen oxides decreased by up to 35% and PM decreased by up to 90%. In comparison with 100% FAME fuel, nitrogen oxides decreased by 45% and PM decreased by 45%. On the other hand, fuel consumption and the production of carbon monoxide increased by up to 40% in comparison with the diesel oil. However the used tractor engine Zetor 1204 was not using the oxidation catalyst, so it can be assumed, that the increased emissions of CO would be consumed during reaction in the catalyst.

The use of wood waste for energy purposes, such as the production of biofuels derived from lignocellulose, is a promising alternative and has a great potential for usage in combustion engines. It is possible to use biobutanol as an additive in fuel for the combustion engine, particularly in lower concentration.

Table 6. Measuring Points of the NRSC Test for 10 BUT Fuel

Speed	Torque (%)	Weight (-)	Speed (1/min)	Torque (Nm)
Rated	100	0.15	2201.6 ± 5.644	194.37 ± 1.634
Rated	75	0.15	2197.3 ± 5.657	139.44 ± 1.807
Rated	50	0.15	2196.5 ± 3.265	92.61 ± 1.414
Rated	10	0.10	2196.1 ± 6.514	19.26 ± 0.263
Intermediate	100	0.10	1518.1 ± 5.433	263.65 ± 8.449
Intermediate	75	0.10	1514.2 ± 4.449	204.54 ± 8.007
Intermediate	50	0.10	1515.0 ± 3.703	133.28 ± 3.463
Idle Run	-	0.15	726.0 ± 1.924	0.00 ± 0.000

Table 7. Results of the NRSC Test for Tested Fuels

Fuel	Specific perform- ance (kW)	Brake specific fuel consumption (g/kWh)	CO ₂ (g/kWh)	HC (g/kWh)	NO (g/kWh)	PM (g/kWh)	CO (g/kWh)
100_FAME	27.91	366.3	1306.2	0.036	15.58	0.048	1.886
Diesel - EN 590	27.88	325.3	1344.1	0.045	13.48	0.364	3.486
10_BUT	24.72	418.0	1069.7	0.039	9.40	0.043	2.844
30_BUT	23.38	441.1	1139.2	0.057	9.68	0.030	3.283
50_BUT	22.62	450.7	1116.8	0.063	8.73	0.026	4.972

A more economical option is to use mixed fuel (oil and biobutanol). This is preferable to performing demanding esterification or to restructure the vehicle in order to burn the oil in its pure form, both of which risk damaging the combustion engine, in particular, the injection pump and injectors.

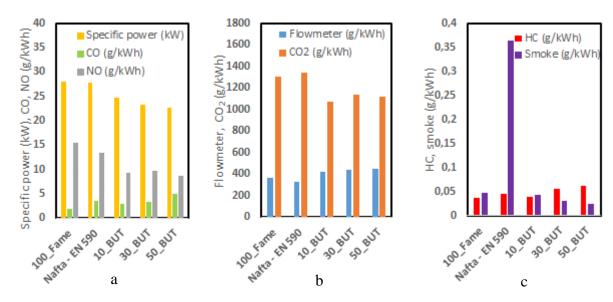


Fig. 5. Results of the NRSC test: a) specific fuel, CO and NO, b) flowmeter and CO₂, c) HC and PM

CONCLUSIONS

- 1. The use of a higher proportion of biobutanol in fuel resulted in a significant decrease of performance parameters (by up to 20 %) but also resulted in an increase of torque reserve (by up to 10 %).
- 2. Using a higher proportion of biobutanol in fuel resulted in decreased production of carbon dioxide (by up to 15 %), nitrogen oxides (by up to 35 %), and PM (by up to 90 %).
- 3. A higher proportion of biobutanol in fuel resulted in increased production of hydrocarbons (by up to 40%), carbon monoxide (by up to 45%), and fuel consumption (by up to 40%) within the NRSC test.
- 4. The usage of biobutanol as an additive in FAME and especially in oils significantly decreased the viscosity and density of the fuel (while using 50% biobutanol the fuel meets the standard EN 14214).

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