

Do Bio-Derived Liquid Transportation Fuels have Oxygen and Carbon-Dioxide Saving Potential throughout their Combustion? - Theoretical Calculations

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Abstract

The transport sector's energy consumption is forecasted to increase worldwide in the future. Due to this raising tendency, environment will be loaded and polluted throughout pollution coming from the transport sector. Biofuels are judged as questionable whether they can be useful regarding their usage. In the following study, two rarely investigated parameters like oxygen consumption and carbon-dioxide emission will be analysed during the theoretical combustion process of fuels. In case of these parameters, biofuels can have advantages compared to those of fossil fuels. The reduction potential can be higher if the calculation is related in addition to potentials formats during the life of (fuel) plants as well.

Keywords: Oxygen Saving Potential; Carbon-Dioxide Saving Potential; Fossil Fuels; Renewable Fuels; Theoretical Calculations

Abbreviations

CO: Carbon-Monoxide Molecule; HC: Hydrogen-Carbon; C_nH_m : Hydrogen-Carbon Molecule with a Certain Amount of Carbon and Hydrogen; O_2 : Oxygen Molecule; CO_2 : Carbon-Dioxide; H_2O : Water Molecule; $C_xH_yO_z$: Hydrogen-Carbon-Oxygen Molecule with a Certain Amount of Carbon, Hydrogen and Oxygen; Q: A Sign of Heat; C_8H_{18} : Octane; C: Carbon Atom; H: Hydrogen Atom; O: Oxygen Atom; $C_{16}H_{34}$: Cetane (Hexadecane); C_2H_6O : (Bio)Ethanol ((Bio)Ethyl-Alcohol); $C_{19}H_{34}O_2$: Methyl Oleate; ρ_g : Density of Gasoline; ρ_e : Density of Ethanol; ρ_d : Density of Diesel; ρ_b : Density of Biodiesel; E10: A Fuel Blend of Gasoline and Bioethanol in which Bioethanol is Blended in 10 V/V %; B7: A Fuel Blend of Diesel and Biodiesel in which Biodiesel is Blended in 7 V/V %; Eq.: Equation

Introduction

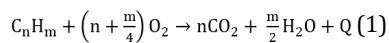
The transport sector's energy consumption is forecasted to increase worldwide in the future. Due to this raising tendency, environment will be loaded and polluted throughout pollution coming from the transport sector [13-16]. According to [18] bio-derived energy will also be used increasingly by 2050. The share of renewable energy sources in the transportation sector may be slightly below 5 % globally [13] while that is calculated significantly higher in Europe [17] in the long term, while another study suggests that the share of biofuels in transport will be even higher [15]. There are many alternative energy sources in the sector, which can be a solution instead of the fossil sources. The biofuels can be found among these opportunities [19]. The aim of biofuel's usage is primarily the diversification of fuel resources, preservation of fossil stocks and keeping energy security [20,21]. Requirements regarding utilization rate of the renewable

energy in the European Union are set out in [22]. They are judged as questionable whether they can be useful regarding their usage. Their properties are different from those of standardised fossil origin fuels. After that, to mention their effect on emission of an internal combustion engine because it is a mixed situation. It means that regarding certain components they have advantages, so these components like CO, HC decrease using biofuel and other emission-components for example particulate mass increases [23,24].

In the following study, two rarely investigated parameters like oxygen consumption and carbon-dioxide emission will be analysed during the theoretical combustion process of fuels. In case of these parameters, biofuels can have advantages compared to those of fossil fuels. Oxygen production and carbon-dioxide absorption of plants during their life can be another advantage factor of renewable fuels but this will not be in focus in this work.

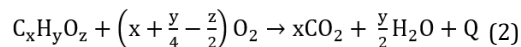
Theoretical combustion process of hydrocarbons

Liquid transportation fuels used in the transportation sector consist of hydrocarbons. The general chemical equation for the oxidation of hydrocarbons is as follows [5]:



Expressed in words this equation: A certain amount of oxygen is needed to burn a hydrocarbon, containing a given amount of carbon and hydrogen. The oxidation process also generates a certain amount of carbon dioxide, water and heat.

If the hydrogen-carbon contains additional oxygen the oxidation process seems to be the following [2,3]:

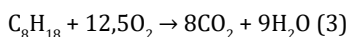


If a molecule built up of carbon-hydrogen-oxygen is intended to combust, theoretically it requires lower amount of oxygen and the quantity of produced carbon-dioxide depends only on the quantity of carbon in the molecule according to equation (2).

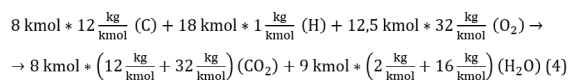
Calculation of O₂ consumption and CO₂ emission generated during combustion of liquid transportation fuels

Theoretical combustion process of gasoline

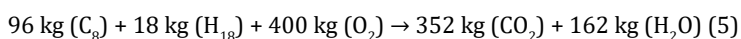
According to [6], fossil gasoline consists of 200 - 300 types of different hydrocarbons. However, this needs to be simplified for our calculation. In the following, gasoline is replaced by octane [7]. Using the theoretical oxidation process of octane, arises equation (3):



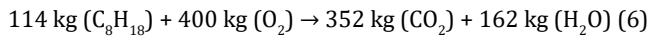
This equation is based on amount of substance (mol, kmol). To be manageable for us, we need to convert it to a mass base. For this, the molar mass of each chemical element is used, which values are as follows: C = 12 kg/kmol, H = 1 kg/kmol, O = 16 kg/kmol [5]. Based on equation (1) it can be explicated:



By multiplying the factors, it will become the following equation:



Combining carbon and hydrogen the final equation is as follows:



The two specific factors per unit mass of fuel can already be determined:

Oxygen consumption: The left side of the equation (6) shows the theoretical oxygen demand on a mass basis. To burn octane (C₈H₁₈) per unit mass, therefore:

$$\frac{400 \text{ kg (O}_2)}{114 \text{ kg (C}_8\text{H}_{18})} = 3.5 \frac{\text{kg (O}_2)}{\text{kg (C}_8\text{H}_{18})} \quad (7)$$

3.5 kg of O₂ is required. If the value 3.5 would not be immediately recognizable, it can be checked if we calculated correctly. To do this, take the mass-based ratio of air to oxygen content in the air [5]. This is shown by equation (8):

$$\frac{m_{air}}{m_{O_2}} = \frac{1}{0,232} \rightarrow m_{air} = 4.31 * m_{O_2} \quad (8)$$

Based on equations (7) and (8) equations the theoretical specific air demand is:

$$3.51 \frac{\text{kg (O}_2)}{\text{kg (C}_8\text{H}_{18})} * 4.31 = 15.1 \frac{\text{kg (air)}}{\text{kg (C}_8\text{H}_{18})} \quad (9)$$

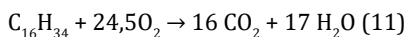
This is called theoretical or stoichiometric air demand. It means that 15.1 kg of air is required for the theoretical oxidation of 1 kg of octane.

The CO₂ emissions are also based on equation (6) per unit mass of fuel:

$$\frac{352 \text{ kg (CO}_2)}{114 \text{ kg (C}_8\text{H}_{18})} = 3.09 \frac{\text{kg (CO}_2)}{\text{kg (C}_8\text{H}_{18})} \quad (10)$$

Theoretical combustion process of diesel

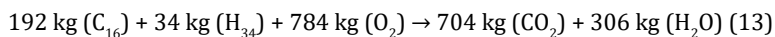
According to [6], diesel consists of many more types of different hydrocarbons than gasoline consisting of 200-300 different. However, for our calculation, this needs to be simplified in the same way. In the following, the diesel is replaced by cetane (hexadecane) [7]. Based on the equation (1) theoretical oxidation process of hexadecane is the following:



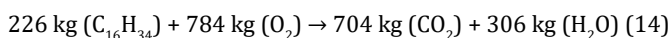
This equation is based on amount of substance (mol, kmol) as well. To be manageable for us, we need to convert it to a mass base. The next equation can be got using the molar mass values of the different chemical elements:

$$\begin{aligned} & 16 \text{ kmol} * 12 \frac{\text{kg}}{\text{kmol}} (\text{C}) + 34 \text{ kmol} * 1 \frac{\text{kg}}{\text{kmol}} (\text{H}) + 24,5 \text{ kmol} * 32 \frac{\text{kg}}{\text{kmol}} (\text{O}_2) \rightarrow \\ & \rightarrow 16 \text{ kmol} * \left(12 \frac{\text{kg}}{\text{kmol}} + 32 \frac{\text{kg}}{\text{kmol}} \right) (\text{CO}_2) + 17 \text{ kmol} * \left(2 \frac{\text{kg}}{\text{kmol}} + 16 \frac{\text{kg}}{\text{kmol}} \right) (\text{H}_2\text{O}) \quad (12) \end{aligned}$$

By multiplying the factors in equation (12), it will become the following equation:



After combining the carbon with the hydrogen arises:



The two specific factors per unit mass of fuel can already be determined:

Firstly, oxygen consumption: The left side of equation (14) shows the theoretical oxygen demand on a mass basis. To burn hexadecane ($C_{16}H_{34}$) per unit mass:

$$\frac{704 \text{ kg } (O_2)}{226 \text{ kg } (C_{16}H_{34})} = 3.1 \frac{\text{kg } (O_2)}{\text{kg } (C_{16}H_{34})} \quad (15)$$

3.1 kg of O_2 is required. Air consumption can be calculated knowing the oxygen demand with the help of the mass-based ratio of air to oxygen content in the air [5]. It is shown in equation (16):

$$\frac{m_{air}}{m_{O_2}} = \frac{1}{0,232} \rightarrow m_{air} = 4.31 * m_{O_2} \quad (16)$$

Based on equations (15) and (16), the theoretical specific air demand is:

$$3,1 \frac{\text{kg } (O_2)}{\text{kg } (C_{16}H_{34})} * 4,31 = 13.36 \frac{\text{kg } (air)}{\text{kg } (C_{16}H_{34})} \quad (17)$$

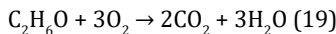
This is also called theoretical or stoichiometric air demand. It means that the theoretical oxidation of 1 kg of hexadecane ($C_{16}H_{34}$) requires 13.36 kg of air.

CO_2 emissions are also based on equation (14) per unit mass of fuel as follows:

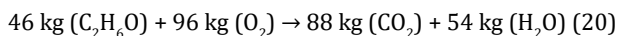
$$\frac{704 \text{ kg } (CO_2)}{226 \text{ kg } (C_{16}H_{34})} = 3.1 \frac{\text{kg } (CO_2)}{\text{kg } (C_{16}H_{34})} \quad (18)$$

Theoretical combustion process of bioethanol

The bio-based blending component of gasoline is ethanol [4]. Ethanol is built up carbon, hydrogen and oxygen with the molecular formula C_2H_6O [4]. Chemical process of its oxidation can be described with the help of the equation (2). Equation (19) shows the result:



Equation (19) has to be transferred to a mass based one. The transfer is no longer detailed, can be got:



On the basis of equation (20) the two key parameters can be determined as follows:

Oxygen consumption can be calculated if the left side of equation (19) is used. To burn ethanol per unit of fuel mass can be done:

$$\frac{96 \text{ kg } (O_2)}{46 \text{ kg } (C_2H_6O)} = 2.09 \frac{\text{kg } (O_2)}{\text{kg } (C_2H_6O)} \quad (21)$$

If 1,74 kg of O_2 available. The theoretical specific air demand seems to be:

$$2.09 \frac{\text{kg } (O_2)}{\text{kg } (C_2H_6O)} * 4.31 = 9 \frac{\text{kg } (air)}{\text{kg } (C_2H_6O)} \quad (22)$$

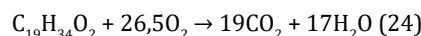
That is, the theoretical oxidation of 1 kg of ethanol requires 9 kg of air.

The CO_2 emission related to one unit of mass of fuel develops based on equation (19):

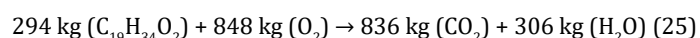
$$\frac{88 \text{ kg } (CO_2)}{46 \text{ kg } (C_2H_6O)} = 1.91 \frac{\text{kg } (CO_2)}{\text{kg } (C_2H_6O)} \quad (23)$$

Theoretical combustion process of biodiesel

Biodiesels are produced from fatty acid esters using alcohols. Their typically chain length is C_{14} - C_{22} . [1]. Biodiesels have been intensively studying as an alternative fuel option for compression ignition engines. Methyl oleate ($C_{19}H_{34}O_2$) is frequently in focus during detailed chemical kinetics research [2,3]. In the following, methyl oleate will be used in the calculation. On the basis of equation (2) can be written:



It is shaped so on a mass basis:



Based on equation (25) our two key parameters can be determined as follows:

Oxygen consumption: to burn theoretically a unit mass of $C_{19}H_{34}O_2$:

$$\frac{848 \text{ kg } (O_2)}{294 \text{ kg } (C_{19}H_{34}O_2)} = 2.88 \frac{\text{kg } (O_2)}{\text{kg } (C_{19}H_{34}O_2)} \quad (26)$$

2,76 kg of O_2 is needed. In parallel with O_2 consumption the specific air demand arises:

$$2.88 \frac{\text{kg } (O_2)}{\text{kg } (C_{19}H_{34}O_2)} * 4.31 = 12.41 \frac{\text{kg } (air)}{\text{kg } (C_{19}H_{34}O_2)} \quad (27)$$

For theoretic oxidation of a unit mass of methyl oleate 12.41 kg of air is needed.

The CO_2 emissions are also according to equation (24) per unit mass of fuel as follows:

$$\frac{836 \text{ kg } (CO_2)}{294 \text{ kg } (C_{19}H_{34}O_2)} = 2.84 \frac{\text{kg } (CO_2)}{\text{kg } (C_{19}H_{34}O_2)} \quad (28)$$

Results and Discussion

Specific O_2 consumption and CO_2 emission of fossil and bio-derived liquid transportation fuels

Based on the calculation's results above a summary of the most important values can be seen in table 1. Because of the bounded oxygen content of the biofuels their theoretical oxygen demand is lower than those of the fossil fuels. That is the situation in case of the stoichiometric air demand. And this is the case as far as specific CO_2 emission is concerned.

	Oxidation of gasoline	Oxidation of diesel	Oxidation of ethanol	Oxidation of biodiesel
Theoretical O_2 consumption [kg O_2 /kg fuel]	3.5	3.1	2.09	2.88
Stoichiometric air demand [kg air/kg fuel]	15.1	13.36	9.0	12.41
Theoretical CO_2 emission [kg CO_2 /kg fuel]	3.09	3.1	1.91	2.84

Table 1: Theoretical data of O_2 consumption and CO_2 emission during combustion of different fuels.

Both in the European Union and in Hungary, standards set the composition and physical and chemical properties of fuels that can be sold at petrol stations. Bioethanol [10] is the blending component for gasoline [11] and biodiesel [9] for diesel [8]. Bioethanol is blended

at 10 V/V % [11], biodiesel is blended at 7 V/V % [8] with their fossil counterpart. In the following, the O₂ consumption and CO₂ emission will be calculated taking into consideration the E10 and B7 are blends of fuels for those one by one this calculation has been made. Equations no. (29)-(36) show the results, which are also summarized in table 2.

	E10	B7
O ₂ consumption [kg O ₂ /kg fuel blend]	2.53	2.65
CO ₂ emission [kg CO ₂ /kg fuel blend]	2.24	2.62

Table 2: O₂ consumption and CO₂ emission values regarding the fuel blends.

O₂ demand

$$\text{O}_2 \text{ consumption}_{\text{E10}} = 90 \text{ V/V \%} * \rho_g * \text{Theoretical O}_2 \text{ consumption of gasoline} + 10 \text{ V/V \%} * \rho_e * \text{Theoretical O}_2 \text{ consumption of ethanol} \quad (29)$$

$$\text{O}_2 \text{ consumption}_{\text{E10}} = 0.9 * 0.75 * 3.5 + 0.1 * 0.79 * 2.09 = 2.365 + 0.165 = 2.53 \quad (30)$$

$$\text{O}_2 \text{ consumption}_{\text{B7}} = 93 \text{ V/V \%} * \rho_d * \text{Theoretical O}_2 \text{ consumption of diesel} + 7 \text{ V/V \%} * \rho_b * \text{Theoretical O}_2 \text{ consumption of biodiesel} \quad (31)$$

$$\text{O}_2 \text{ consumption}_{\text{B7}} = 0.93 * 0.85 * 3.1 + 0.07 * 0.88 * 2.88 = 2.45 + 0.18 = 2.65 \quad (32)$$

CO₂ emission

$$\text{CO}_2 \text{ emission}_{\text{E10}} = 90 \text{ V/V \%} * \rho_g * \text{Theoretical CO}_2 \text{ emission of gasoline} + 10 \text{ V/V \%} * \rho_e * \text{Theoretical CO}_2 \text{ emission of ethanol} \quad (33)$$

$$\text{CO}_2 \text{ emission}_{\text{E10}} = 0.9 * 0.75 * 3.09 + 0.1 * 0.79 * 1.91 = 2.086 + 0.15 = 2.24 \quad (34)$$

$$\text{CO}_2 \text{ emission}_{\text{B7}} = 93 \text{ V/V \%} * \rho_d * \text{Theoretical CO}_2 \text{ emission of diesel} + 7 \text{ V/V \%} * \rho_b * \text{Theoretical CO}_2 \text{ emission of biodiesel} \quad (35)$$

$$\text{CO}_2 \text{ emission}_{\text{B7}} = 0.93 * 0.85 * 3.1 + 0.07 * 0.88 * 2.84 = 2.45 + 0.175 = 2.62 \quad (36)$$

where: $\rho_g, \rho_e, \rho_d, \rho_b$ - density of gasoline, ethanol, diesel, biodiesel [kg/dm³].

Reduction potential in O₂ consumption throughout theoretical combustion of renewable fuels as a blending component

With the help of the values calculated above further calculations have been made on a theoretical basis. The aim of this calculation is showing the reduction potential of biofuels regarding our two key parameters. It is not aimed to give an exact result, but only to illustrate the order of magnitude. During the calculation the next steps have been involved:

- Statistics for engine fuel quantity for 2019 in Hungary have been taken from [12];
- In the first step of calculation it is assumed, that these fuels are exclusively fossil. O₂ consumption of fuels are calculated with the specific figures taken from table 1. O₂ consumption regarding “Fossil fuel total” has been got;
- In the second calculation it is assumed that these fuels are real ones, so the blends. O₂ consumption of fuel blends are calculated with the specific figures taken from table 1. O₂ consumption regarding “E10+B7 total” has been got;
- Relative change in O₂ consumption is also shown in table 3;

Fuel	Fuel consumption [kg]	Oxygen-consumption [kg]
Gasoline	1.114.907.107	3.902.174.874
Diesel	2.068.402.409	6.412.047.468
Fossil fuel total		10.314.222.342
E10	1.114.907.107	2.820.714.980
B7	2.068.402.409	5.481.266.384
E10+B7 total		8.301.981.364
Relative change in oxygen consumption:		-19.5%

Table 3: Reduction potential in O₂ consumption.

- The differences in lower heating value and combustion properties between fossil and biofuels have not been taken into account. Considering these the relative value may be lower.

Reduction potential in CO₂ emission throughout theoretical combustion of renewable fuels as a blending component

Calculation process introduced in the previous section has been carried out in the same way in this subsection. The relative change is 23% regarding CO₂ emission.

Fuel	Fuel consumption[kg]	Emission of carbon-dioxide [kg]
Gasoline	1.114.907.107	3.902.174.874
Diesel	2.068.402.409	6.412.047.468
Fossil fuel total		10.314.222.342
E10	1.114.907.107	2.497.391.920
B7	2.068.402.409	5.419.214.312
E10+B7 total		7.916.606.232
Relative change in carbon-dioxide emission:		-23%

Table 4: Reduction potential in CO₂ emission.

The calculated reduction potentials do not take many things into account, but nonetheless they seem to be attractive, also because the blending rate of renewable fuels are low. This calculation is concerning only directly the combustion process of fuel and does not deal with the potentials format during the life of plants from which fuel are made.

Conclusion

As a result of the study introduced above can be concluded as follows:

- Theoretical combustion process of fuels with bio origin requires less O₂ and emits less CO₂;

- Reduction potential regarding these two key parameters is a significant value (relative change) calculated with a simplified calculation method and taking into consideration
 - An amount of fuels related to Hungary in 2019;
 - And low blending rates (E10 and B7);
- The reduction potential can be higher if the calculation is related in addition to potentials formats during the life of (fuel) plants as well.

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