TRANSESTRIFICATION OF BIOOILS, YES BUT WHY?

Lech J. Sitnik

Wroclaw University of Technology Faculty of Mechanics Institute of the Construction and Operation of the Machines Lukasiewicza 7/9 Street, 50-371 Wrocław (Poland) tel./(fax) +48 71 347 79 18 e-mail: lech.sitnik@pwr.wroc.pl

Abstract

This paper presents a novel way of utilizing alcohols as fuels for a diesel engine. It is proposed to use heavy alcohols as a mix with vegetable oils and conventional diesel fuel. It is presented the another way to use alcohols. Namely the use of heavy alcohols as a solvent for vegetable oil (named the biomix or BM) and after the obtainment of the thickness which would be approximate to diesel fuel, mixing the biomix with diesel fuel to obtained biomixdiesel (BMD). This solution will be shown for example with butanol as heavy alcohol, rape oil as vegetable oil and conventional diesel fuel. The investigations are carried out with a simple diesel engine on the engine test bed. Main parameters of engine (power output, torque, specifically fuel consumption) and the main exhaust gas component (in this case CO, NO_{x} , PM) will be investigated. There were better results achieved than one expected. Opposed to existing experiences, the maximum of power output and the torque of engine are higher in the whole range of the rotatory speed of the engine crankshaft when the engine biomixdiesel (BMD) is reinforced. The addition of the component biomix to fuel influences the specific fuel consumption. Generally with the larger part of the component biomix the specific fuel consumption grows. Because the power of engine also grows up one should expect that in exploitation the specific fuel consumption should not increase. Transestrification process in the proposed solution does not appear. This has large economic meaning. The investment amount (the transestrification plant) is not necessary. The power consumption to get fuel is lower. Vegetable oils are fully used (glycerin is not produced). BMD has stable parameters. The usage of existing infrastructure to this transportation is enough. Very important is that this fuel could be used to reinforce old, existing now and the future diesel engines. The production of butanol is known. It will be interesting to use for the production an electrolysis process, especially in the proposed new plant where the electrolysis process is connected with the process to get the electrical energy from byproducts of electrolysis (i.e. hydrogen and oxygen) in the fuel cell. It seems to be more efficient. The possibility to get butanol from ethanol gives a very good perspective for the use of ethanol from today's overproduction and moreover without the essential change of infrastructure.

Keywords: transport, diesel engines, fuels, alternative fuels, biofuela

1. Introduction

The EU road transport sector accounts for more than 30% of the total energy consumption in the Community. It is 98% dependent on fossil fuels with a high share of imports and thus extremely vulnerable to oil market disturbance. The growing transport sector is considered to be one of the main reasons for the EU failing to meet the Kyoto targets. It is expected that 90% of the increase of CO_2 emissions between 1990 and 2010 will be attributable to transport [1].

Europe has defined ambitious targets for development of biofuels. Thus the requirement of the European Union, that:

- till year 2020,
- the energy consumption has to be lowered about 20%, and

- 20% fuel has to come from renewable natural resources (in case of engine fuels it will be 10%), are fully comprehensible and must be fulfilled.

An ambitious and achievable vision for 2030 is that up to one quarter of the EU's transport fuel needs could be met by clean and CO₂-efficient biofuels.

The EU has a significant potential for the production of biofuels. It is estimated that between 4 and 18% of the total agricultural land in the EU would be needed to produce the amount of biofuels to reach the level of liquid fossil fuel replacement required for the transport sector in the Directive 2003/30/EC [1].

A substantial part will be provided by a competitive European industry, using a wide range of biomass resources, based on sustainable and innovative technologies. Biofuel development will create opportunities for biomass providers, biofuels producers and the automotive industry. Also, the European technology will be used in 2030 in many countries exporting biofuels to Europe.

The aim is to improve European domestic energy security, improve the overall CO_2 balance and sustain European competitiveness. The question is only how?

Biofuels that exist in the market or are in phase of investigations are:

- alcohols (first of all ethanol),
- vegetable oils and from these oils fatty acid (methyl or ethyl) esters,
- synthetic hydrocarbons (from the synthesis gas coming from the biomass).

Alcohols have the biggest chance to be the engine fuel. Second place required synthetic hydrocarbons from the biomass. Vegetable oils can be only (demanded) ingredients to the engine fuels because of agricultural limits (we have too small areas to grow the oil plants). Opposite to them obtaining of alcohols has very rich sources (not only biomass directly but organic part of communal waste or settings of waste water for example too).

Rich sources of input material to obtain of ethanol bring world wide hope with is connected with the use of ethanol as a biofuel and this is the case especially in Europe. The reason for this is comprehensible:

- in every European country the technology of the production of ethanol from biomass is well-known,
- in every European country there is the overproduction of ethanol,
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- in every European country there is the excess of wastes which can be used to the production of the ethanol,
- every European country imports liquid fuels excessively especially engine fuels,
- every European country has the unemployment problem.

Usual technologies are known but they are in development too.

For biochemical-conversion technologies, a major R&D focus is on improving pretreatment technology for breaking hemicellulose down to component sugars and developing more cost-effective cellulase enzymes (biocatalysts) for breaking cellulose down to its component sugar [2].

Another key enabling technology is the engineering of microorganisms and enzymes that can efficiently convert the complex cellulosic wastes to simple sugars and then to ethanol or chemical building blocks.

But the ethanol is not good as engine fuels. There is the conception of using of the ethanol in specially adapted spark ignition engines, like in Brazil or Sweden (with low efficiency of this art of engines) or in special diesel engines, like a SCANIA in Europe (in this case with higher efficiency). The efficiency of engines is a major reason to use (especially in Europe) more and more diesel engines. This has an impact of consumption of main fuel art. For example consumption of diesel fuel in Europe is greater as possibility to obtain this fuel from crud oil. This develops the situation that in Europe we have "overproduction" of petrol. But proportion in fuel production must be kept i.e. petrol consumption must be higher. In any European country nowadays also petrol price is lower than diesel fuel.

Also we have a situation in which we have the overproduction of ethanol (as the fuel biocomponent, too) and we started to R&D works on technologies which will allow this overproduction to be greater.

2. Problem

In Europe (and worldwide) there is overproduction of biomass and overproduction of light alcohols especially ethanol. That is the best confirmation of fact that ethanol is not acceptable fuel. Mixing of ethanol with hydrocarbon fuels is very problematic. Eethanol as a fuel ingredient has a limited (by diesel fuel practically to 10%) application. Ethanol is hydro filing what changes fuel properties. Energy contents in ethanol are half as high as for example petrol. The spark ignition engines where ethanol can be used as fuel are lower efficiency than diesel engines, etc.

Main problem with introduction of ethanol is that ethanol can be mixed on large scale only with petrol. In other case ethanol can be used as fuel only in the special engines. And these engines in Europe are not in use (today we use more and more diesel engines). The situation is that the ethanol from the nowadays overproduction can be used only as an ingredient to petrol which is today in the overproduction as well. In another case all engines existing today in exploitation must be changed. That is technically possible but it needs time, money and efforts. All this has no sense because it is not necessary.

3. Problem solution

The problem mentioned above will be solved in case of the introduction of fluids coming from biomass to exploitation. They must be compatible with conventional or synthetic hydrocarbons. One of these fluids are heavy alcohols (which contain more than 2 atoms of carbon in a molecule). Especially butanol [3] is good here.

Properties of butanol as engine fuel or an engine fuel ingredient are very good - opposite to the ethanol [3, 4]. All these problems that come from the ethanol introduction as an engine fuel do not exist with the butanol.

The energy content of butanol is almost the same as petrol. Butanol mix well (in any proportion) with all hydrocarbon fuels especially with diesel fuel. Butanol is hydrophobic so properties of fuel do not change for a long time. Hydrocarbon mix with butanol (or butanol itself) can be used in today's existing engines.

Butanol can be produced from feedstock coming from renewable sources. In this case butanol is called as a biobutanol.

Biobutanol can be produced in two main technological processes:

Directly from biomass. In this case biobutanol can be produced by fermentation of biomass in A.B.E. process. The process uses the bacterium *Clostridium acetobutylicum*. (Currently new bacteria's are still searching). Difference to ethanol production is primarily in fermentation of feedstock - producing of butanol rather than ethanol causes butanol fermentation and does not change distillation. Feedstocks are the same as for ethanol - energy crops such as sugar beetroots, sugar cane, corn grain, wheat and cassava as well as such as straw and corn stalks.

According to DuPont existing bioethanol plants cost of change to biobutanol production can be retrofitted [3].

However analysis of possibility of biobutanol production shows that nowadays technologies are not effective. During production process are formed a lot of byproducts (for example acetone) so that obtaining of biobutanol from biomass is relatively low. Production process is by this complicated and not friendly for environment. Situation can be changed in case of introduction of new bacteria first from all genetically modified ones. Of course introduction of this process needs new infrastructure expenses.

Not without meaning is fact that existing infrastructure for ethanol production would not be used. Today's overproduction of ethanol from existing plants also would not be used too.

Another path to biobutanol production is electrolysis of (bio) ethanol.

Electrolysis goes according to the chemical eqation:

 $2C_2H_5OH + 2C_2H_5OH \rightarrow 2C_4H_9OH + 2H_2 + O_2.$

This possibility of biobutanol forming is the most effective today. Technology of ethanol production is relatively simple and is worldwide known. To implement of conversion of ethanol in to butanol a new designed plant is proposed, where electrolysis process is directly connected with fuel cell for production of electricity.

Generally plant concept is showing on the Fig. 1.

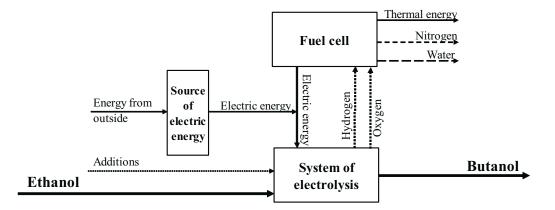


Fig. 1. Plant concept to obtain butanol from ethanol

Electrical energy needed to electrolysis process comes from fuel cell. And byproducts of ethanol electrolysis (that is hydrogen and oxygen) are led to fuel cell where electrical energy is now produced. So with conversion of ethanol to butanol only energy to cover all electrical losses is needed. This solution permits butanol production with very low energy consumption. External energy can come from removable sources like solar energy (wind or water energy, too).

Synthesis of butanol form ethanol in electrolysis process is therefore possible but relatively not much recognized. It must be carefully researched.

Very important is, that ethanol from today's overproduction can be transformed into butanol.

Butanol is a very good solvent. This property will be used to prepare biofuels as a mix of (bio) butanol and vegetable oils. The density of vegetable oils, useful for fuels, is generally higher than the diesel fuel for example. Butanol density (e.g. 0.8 g/cm^3) is lower than diesel fuel (0.82 to 0.86 g/cm^3 according to EN 590 norm) so that the mix of both ingredients (biooils and butanol) can have the same density like diesel fuel. Further the mix of both bioingredients can be mixed with conventional (or synthetic) diesel fuel to obtain biomixdiesel fuel (BMD).

It will be investigated that the biomix (vegetable oil plus butanol) can be mixed with diesel fuel in any (volumetric) proportion.

Further a new biomixdiesel fuel will be investigated on standard engine bed. Three biomixdiesel fuels were used:

- ON B10 - 90% v/v diesel fuel + 10% v/v biomix (rape oil + butanl),

- ON B20 - 80% v/v diesel fuel + 20% v/v biomix (rape oil + butanl),

- ON B50 - 50% v/v diesel fuel + 50% v/v biomix (rape oil + butanl).

And for comparison

- ON B0 - 100% v/v diesel fuel (EN 590).

Main engine parameters such power output, torque, fuel consumption and emissions (CO - coal monoxide, NO_x - nitrooxides, PM - particle matter) were investigated. A relatively simple engine (without electronic control of injection system) was investigated.

On Fig. 2. it is shown a maximum of engine power output depending on rotation speed of the engine crankshaft with different fuel. Unexpectedly (opposed to existing experiences) maximum power output of engine is higher, in whole range of rotatory speed of engine crankshaft when engine biomixdiesel is reinforced. This is more visible in case of maximum of engine torque (Fig. 3.).

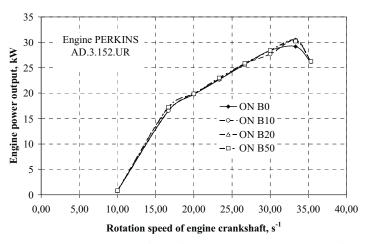


Fig. 2. Maximum of engine power output as a dependant factor of rotation speed of the engine crankshaft with different fuel

It is interesting that maximum torque grows up clearly with the low part of biomix (10%) in fuel. On the other hand the larger part of the component biomix in fuel does not influence the growth of engine torque significantly (Fig. 3).

The addition of the component biomix to the fuel influences the specific fuel consumption. Generally with larger part of component biomix the specific fuel consumption grows but not with all rotation speeds of the engine crankshaft. It is shown in the Fig. 4. For example, with the rotation speed of about 20 s⁻¹ the largest specific fuel consumption appears when the engine is reinforced by conventional diesel fuel. In case of idle speed of engine the specific fuel consumption is obviously the largest (interesting that with the reinforcement of the engine with conventional diesel fuel).

Emission of exhaust gas pollutant is generally smaller with the reinforcement of the engine with biomixdiesel. The more of biomix in fuel the better. Differences are significant, they reach tens of percentages. It is very important (first of all from ecological point of view), that the lowering of the emission of both components of exhaust gases - oxides of nitrogen as well as the particle matter - happens simultaneously.

The investigated diesel engine was relatively old in construction. The obtainment of very good results of lowering emissions can testify that the power supply of biomixdiesel fuel his parameters can get close its parameters to present engines. Of course modern diesel engines which are supplied with biomixdiesel must be better (in all emission parameters) like today.

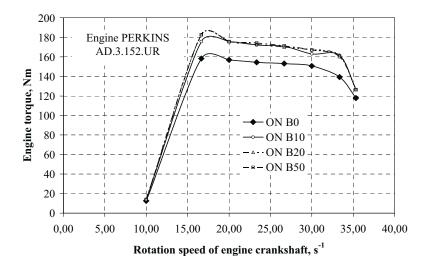


Fig. 3. Maximum of engine torque as a dependant factor of rotation speed of the engine crankshaft with different fuel

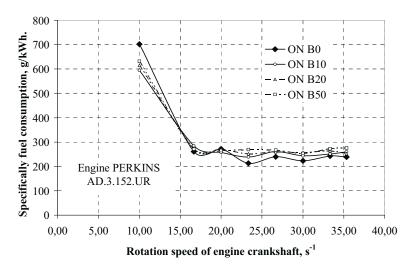


Fig. 4. Maximum of specific fuel consumption as a dependant factor of rotation speed of the engine crankshaft with different fuel

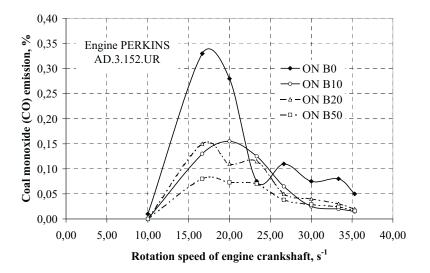


Fig. 5. Coal monoxide (CO) emission as a dependant factor of rotation speed of the engine crankshaft with different fuel

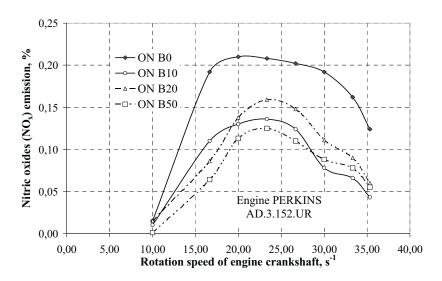


Fig. 6. Nitric oxide (NO_x) emission as a dependant factor of rotation speed of the engine crankshaft with different fuel

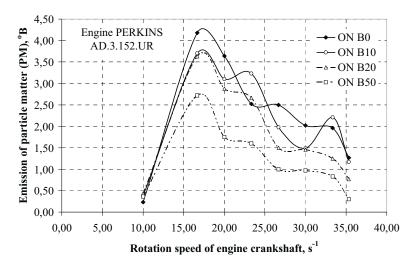


Fig. 7. Emission of particle matter (PM) as a dependant factor of rotation speed of the engine crankshaft with different fuel

4. Conclusion

The increase of prices of fossil fuels for one hand and the environment demand for the other hand lead to the necessity of the introduction of biofuels. Nowadays it is clear to see.

Generally today it is possible in tree ways: the use of alcohols (first of all ethanol) and its mix with petrol, the use of vegetable oils and from these oils the fatty acid (methyl or ethyl) esters and its mix with diesel, the use of synthetic hydrocarbons (from the synthesis gas coming from the biomass) and eventually its mixing with other "classical" hydrocarbons.

It is proposed to use heavy alcohols as a mix with vegetable oils and conventional diesel fuel. It is presented the another way to use alcohols. Namely the use of heavy alcohols as a solvent for vegetable oil (named the biomix or BM) and after the obtainment of the thickness which would be approximate to diesel fuel, mixing the biomix with diesel fuel to obtained biomixdiesel (BMD). This solution was shown with butanol as heavy alcohol, rape oil as vegetable oil and conventional diesel fuel. The investigations were carried out with a simple diesel engine on the engine test bed.

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Very important is that this fuel could be used to reinforce old, existing now and the future diesel engines.

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butanol from ethanol gives a very good perspective for the use of ethanol from today's overproduction and moreover without the essential change of infrastructure.

All this leads to the conclusion that fulfilling of the expected requirements of European Union regarding the biofuels is fully possible.

Literature

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