BIODIESEL FROM AGRICULTURAL RESIDUES

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Abstract

The author of this article has made his library research at Burgenland University of Applied Sciences, Munich University of Applied Sciences, University of Pannonia and Slovak University of Technology. The latter one gave place for the 8-week series of experiment, during which period he produced biodiesel from raw oil and waste cooking oil using different additives. Due to the evaluation of the products it is recognized that due to the costs of catalysts and energy (additionally limited market for side-products) biofuel production is not profitable under today’s economic conditions.

However, for farmers growing oil crops on their undervalued arable land, sharing biorefineries could be a potentially refunded enterprise.

The number of energy crops successfully applied in Hungary are increasing, partly because the European Union is determined to support the domestication of tropical plants on the continent in order to reduce dependence on foreign oil.

With this documentation I’d like to map down some alternative feedstock of the biofuel industry, examining its legal background and chemical procedures, eventually main lines of current scientific researches.

Keywords: renewable energy, biomass, alternative fuels

Összefoglalás

A szerző könyvtári adatkutatását a Burgenlandi Szakfőiskola, Müncheni Főiskola, Pannon Egyetemen Georgikon Karán és Szlovák Műszaki Egyetemen végezte. Az utóbbi volt a helyszíne annak a 8 hetes kísérlet-sorozatnak, melynek során nyersolajból és használt sütőolajból biodízelt állított elő különböző adalékanyagokkal. Ezek értékelése szerint a katalizátor anyag és energia költségei miatt jelenleg nem jövedelmező a kisüzemi biodízel termelés, mindazonáltal lehetséges és a közeljövőben minden bizonnyal megtérülő azok számára, akik gazdálkodóként olajnövényeket termesztenek. A Magyarországon eredményesen termeszthető energianövény-fajták skálája folyamatosan bővül, az Európai Unió olajimport-függősége pedig további nemesítéseket, ill. trópusi növények honosítását szorgalmazza.

Ezzel a dokumentációval szerettem volna a bioüzemanyag gyártás alternatív forrásait feltérképezni, törvényi hátterét megvizsgálni és a kémiai eljárásokat, kutatási irányvonalakat számba venni.

Kulcsszavak: megújuló energia, biomassza, alternatív üzemanyagok

Introduction

The world’s immensely growing energy demand asks for new technologies, higher effectiveness from agricultural/industrial production as well as from domestic consumption. Important from both perspective that there are few alternatives for diesel fuel used in transportation and power-machines. One of them is in conventional ignition-engines with little or no conversion capable biodiesel, scientifically FAME (fatty acid methyl esters). This liquid is marked by a heat value lower that petrol-diesel (37 MJ/kg), on the other hand higher cetane number and proportionately reduced pollution.

The overall biodiesel production reaches 31.13 million tones (Wang, 2019). Blends with varying composition (B7, B20, B100) are standardized by ASTM D6751 in North America (BQ 9000 accreditation), EN14214 in Europe. Hungary's biodiesel-norm is equivalent to that of the Union: MSZ/T 2026.

Ground materials are 95 % edible oily seeds (so called „first generation biodiesel"). In the United States it is soybean, in the EU sunflower and rape, in Middle Asia palm and others. Besides the requisition of arable land another negative characteristic is the market interdependence to oil prices.

A different situation is with agricultural residues, and side products of agricultural production such as biomass-type litter, stem, stalk (55% stover of corn yield), vegetable parts, sewage sludge, tankage (tallow and lard from the slaughterhouse). A mighty field of study is represented in non-edible oil seeds, resp. energy crops mostly originated in warm climate, for example: alfalfa, brazil nut, calendula, camelina, castor beans, chinese tallow, diesel tree, cotton, cumin, euphorbia, fenugreek, hemp, jatropha, jojoba, kenaf, costerm, linseed, lupine, macadamia nut, mahua, neem, pongam oil tree, rubber, safflower, sainfoin, sea mango, tung tree, tobacco, vetches.

Transgene technology (GMO) bears a major role in recently developed researches of oil plants (e.g. raising erucic acid carbon chain 22 in rapeseed) and in algae culture tank farming (Acutodesmus dimorphus, U.S. EPA authorized).

Depending on what kind of hybrid species are applied in horticulture, what purpose are they grown for, we can consider oils and fats as side-products of the vegetable production. (Tanács, 2005)

According to a closer definition every damaged, contaminated, economically worthless unit is:

1. primary agricultural waste: left over on the field for efficiency reasons;

2. secondary a. w.: contaminated by pests, cannot be sold as food/fodder;

3. tertiary a. w.: discarding throughout the processing.

World-wide cultivated crops' oil content is listed in *Table 1*.

Table 1: cultivated crops oil content (self-edited)

crops	*oil content, %*
corn	4.4
soybean	22
peanut	47.2
sunflower	45
rapeseed	40-50
poppy seed	43-53

Animals fats whose market value does not gain profit, can be turned feedstock of fuel production. Pig farms realize an average 1:0,4 lean-to-fat ratio, the 110 days pig has nearly 10 % higher. Lard and speck processing generates a wastage of 22-23 % (Faragó, 1996).

The residue-disposal is topic of numerous researchers, including Christine Göbel (FH Münster), Taher Sahlabji (TU Braunschweig), Reinhold Waltenberger (FH Oberösterreich), P. D. Patil (New Mexico State University), C. F. El Sohl (Cairo University), Vivian Feddern (Technical

University of Athens).

One business example for biofuel production BDI Bioenergy AG with 36 million euros total turnover and 14,500 t/a capacity in 2013 (Austrian plant near Graz). Home research programs since 2003: "Waste to Value ", „Multi Feedstock ", Biomass-to-Liquid, bioCRACK, Algae BioTech, etc.

Waste cooking oil serves as main feedstock provided by 170 restaurants and collection boxes. The animal fat processing of the company is authorized by the European Council (EC/92/2005 and EC 142/2011). This contains crushed bones, DAF Dissolved Air Flotation Sludge, HPFL High Protein Fraction Liquid, blood, purtenance, eventually sewage sludge, food waste.

For DIY biodiesel facility Daphne Utilities, Alabama sets an example offering BioPro 190 Equipment for 3000 dollars. The instructions advice 190 grams KOH to 2 gallons of methanol, ending in 10 gallons oil.

The recycling of cooking oil (Waste Vegetable Oil – WVO) is known in Hungary, too, where Rossi Biofuels Ltd. (part of the ENVIEN Group) is partnering the country's oil distributors. The otherwise dangerous domestic waste is given an additional value this way. The author has therefore specifically used it in his experiments.

Materials and Methods

Under strict laboratory conditions 34 samples were produced (listed by *Table 2*). Raw oil and WVO was used as feedstock, for transesterification 99% concentrated sodium hydroxide granule (NaOH), 99.95% concentrated methanol, for the titration isopropanol and bromothymol, for neutralization 90% concentrated sulfuric acid (H_2SO_4). Relations were determined by the following calculation:

Triglycerides of fatty acids are to be converted to mono-alkyl-esters. Based on concentration and molecular weight it is assumed that 30% of a 100 ml oil is saturated hydrocarbons, 50% half-saturated, leaving the rest 20% unsaturated. This 20 % is to be reduced so that the final product is a reaction neutral, homogeneous. The varying feedstock's changing ratio is to be translated by titration process.

Table 2: marking of samples (self-edited)

samples	*marking*
raw oil FAME	B1
raw oil FAME with double catalyst	B2
raw oil FAME with half amount of catalyst	B0
WVO FAME	B3
WVO FAME with double catalyst	B4
WVO FAME with half amount of catalyst	B5
biodiesel: raw oil mixture	80:20, 60:40, 40:60, 20:80
diesel: biodiesel mixture	75:25, 50:50, 25:75
raw oil, diesel, biodiesel	O, D, BD

The analyzation occurs via FTIR spectrometer (Shimadzu IRAffinity) which indicates the absorbance of the samples in different wave (600 to 4000 cm^{-1}). 30 scans pro sample are read through diamante lenses and forwarded by infrared light converting polychromatic beams to monochromatic. The signals are analyzed with the help of LabSolutions IR software. For each wavenumber characteristic pair of molecules ($-CH_{2n}-$, $-CH_2$, -O-C-C, -C-H-R, etc.) presents the examined matter. According to this CH_2 and CH_3 ethyl groups are between 1450 and 2900 cm^{-1} in FAME, that is in biodiesel. The methyl ester double bonds peak at 1740 cm^{-1}, water contamination at 3400 cm^{-1}.

Results

Demonstrating the conversion of raw oil *Figure 1* shows divergence at some points. Raw oil has a significantly higher proportion on elements between 1000 and 1180 cm^{-1}. *Sample 1*'s values rise above the original matter at 1025, 1385, 1441 and from 1500 to 1600 cm^{-1}. These peaks are responsible for the better lubricity and ignition properties of the fuel. Product-oil mixture proves to be a steady middle value as expected.

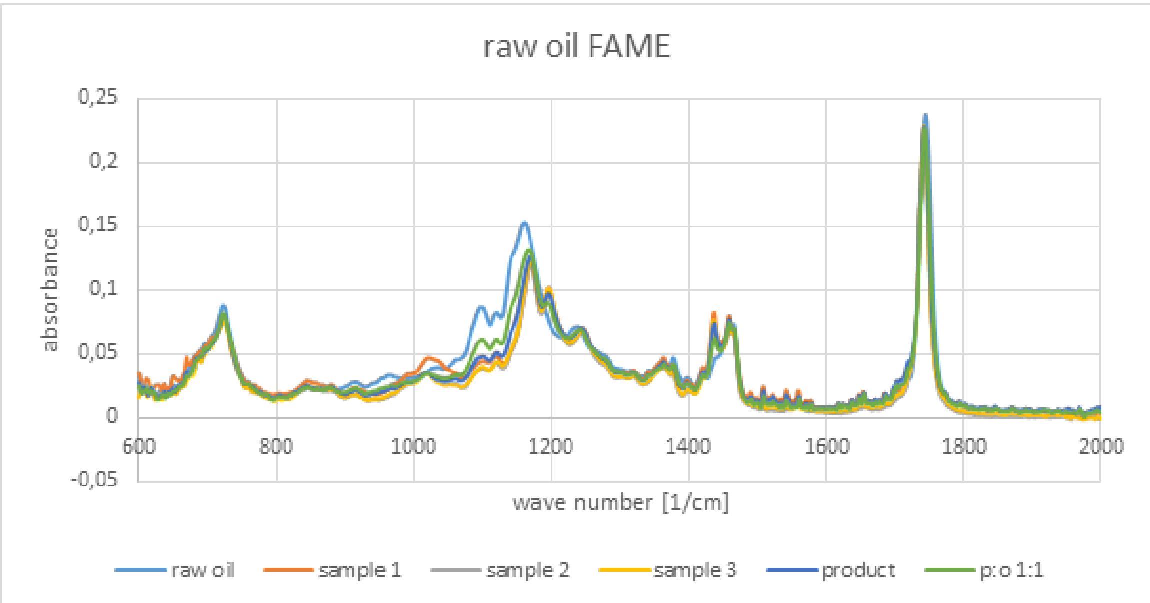

Figure 1: transesterification of unrefined oil (self-edited, Excel, LabSolutions)

The next figure (*Figure 2*) is meant to illustrate the dispersion of fuel mixtures. Transition is visible here as well. Absorbance flattens with improving diesel content. Interestingly mixture 25:75 peaks at 1356, 1450 and 2900 cm^{-1}. This raises questions and leaves space for further investigation in choosing the appropriate blending amongst fuels.

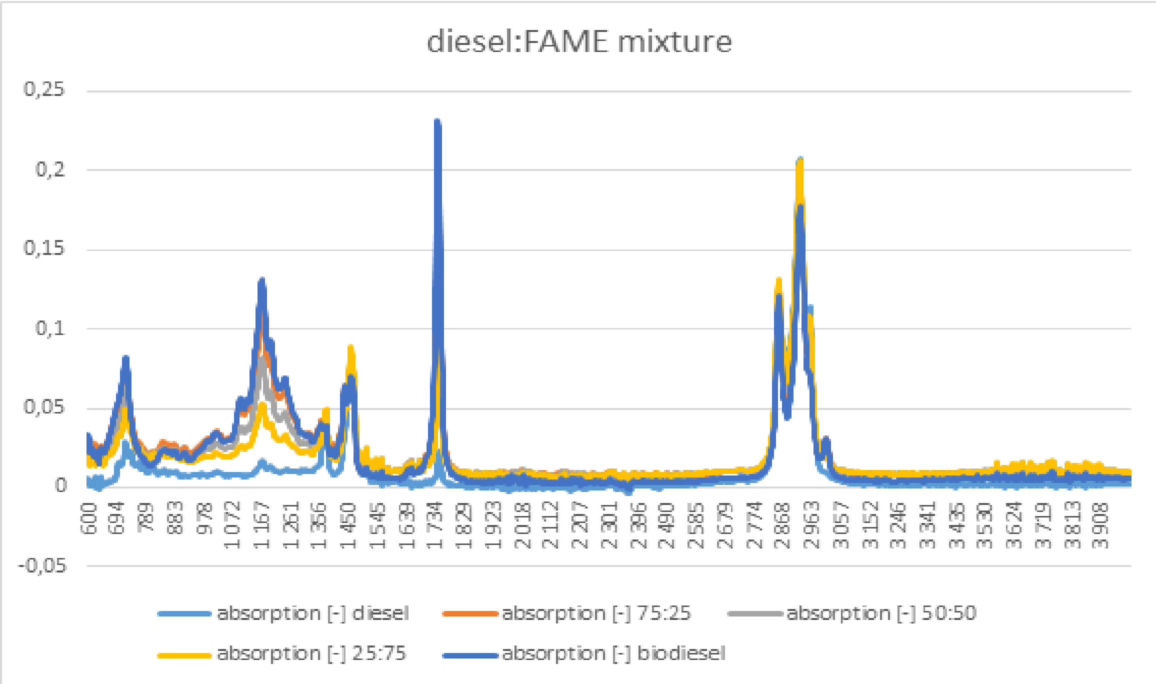

Figure 2: absorbance of biodiesel mixtures (self-edited, Excel, LabSolutions)

The compounds can be identified by a gas chromatograph. Shortly described the working of the equipment is that organic materials are vapored, carried by an inert gas into a heated column where they break up to molecules. A total composition analysis (common for heavy petroleum fractions) is to be accomplished to see what kinds of carbon bonds are generated through the transesterification process. More than 30 organic compounds with molecular weight from 120 to 350 can be quantified in diesel fuel and biodiesel, which includes alkanes, PAHs and alkylated PAHs. However not all of them is known to the software which analyzes the diagram curve of mass to charge ratio. Even vitamin E and squalene was found in the examined biodiesel sample.

Discussion

The purpose of this study was to demonstrate that biodiesel production from vegetable oil is not a complex chemical process. The author’s focus was limited on evaluating differences between used and raw oil in conversion and elementary composition of fuel mixtures. The profitability of biodiesel production is highly dependent on the actual oil prices (86.6 dollars record in 1979) and government subsidies. The future of biofuels is encouraging: alone in the USA 148 plants are working to this date (further 96 under construction) with a total capacity of 1.4 billion gal/a (Howell, 2007).

In the European Union - year 2012 - 26% of biofuels were imported. Through utilization of waste theoretically 16% would be covered of the fuel demand prognosticate for 2030. This would be a 15-billion-euro business with 300.000 people employed (BIOFUELSEUROPE.EU).

A massive cellulosic resource for ethanol industry is portrayed in the throw-away food, package and garden cuttings. According to a 2011 FAO survey food waste takes about 95–115 kg/person, totalized 53 million tons in the EU (Gustavsson et al., 2011). An EUROSTAT survey (2016) estimates 108 million tons animal and vegetable residues in 2010. Within 25.5 million tons from that comes from households, 12 million tons from service and 39 million tons from agriculture. Alone the animal residues are 16.5 million tons. Between the two values stands the European Council report stating 89.3 million tons (Searle, 2013).

Meanwhile the agricultural production is marginally dependent on diesel, e.g. a 7 t/ha wheat yield requires 79 l fuel (Leal-Arcas et al., 2014).

In comparison the latest John Deere 9400 model (15 tons, 12500 ccm engine) has a 76.8 l consumption in an average working hour (TRACTORDATA.COM).

Several ongoing researches are directed to alternative fuels, in the case of biodiesel from residues the approving of lubrication/ignition properties (cloudpoint, cold filter plugging point) could be the key to compete with the regular fuel blends.

The fuel industry is changing fast, keeping up with the trends is substantial to recognize the potential of biofuels in form of public information and political lobby.

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