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CANOLA OIL ELECTOOXITADION ON SMOOTH PLATINUM ELECTRODE

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Abstract

As fuel for fuel cells can be used various substances, but mainly fuel cells are powered by clear hydrogen (or hydrogen obtained from organic substances by reforming process). However, problems with the storage of hydrogen are the reason for the search of new fuels for fuel cells. Due to development of the renewable energy sources, the powering of fuel cells with bio-fuels is very important. Vegetable oil is an alternative fuel for diesel engines and for heating oil burners. Powering high efficiency power sources like fuel cells with renewable fuels (like canola oil) will allow development of renewable energy sources and elimination or reduce of toxic substances emissions. The paper presents the possibility of using canola oil as fuel for direct electricity production. The work shows possible electrooxidation of canola oil emulsion on a smooth platinum electrode in an solution of H_2SO_4. The resulting current density of canola oil electrooxidation reached the maximum level of 8 mA/cm^2. So, the possibility of using canola oil as fuel for direct electricity production has been proved.

Keywords: canola oil, bio-fuel, fuel cell, renewable energy sources, environment engineering

INTRODUCTION

In recent decades the demand of energy has increased significantly. Today's energy production is based on coal, crude oil, natural gas and nuclear energy. In the last decades renewable energy sources also have been fast developing. Various devices using renewable energy sources are used e.g. solar collectors, photovoltaic cells, heat pumps, wind turbines and more. One of these devices is fuel cell (FC). The real efficiency of FCs varies between 40-80% (O'Hayre *et al.* 2005, Stolten 2010). Moreover, zero or low negative influence on the environment and silent operation is what characterizes FCs (Larminie and Dicks 2003). Although the operation principle of a FC has been known since 1939, they still are not widely used, but FCs are successfully used in space industry were costs have not big meaning (Hoogers 2003, Nowicki and Zięcina 1989, O'Hayre *et al*. 2005, Stolten 2010). However, in case of mobile applications, e.g. FCVs (fuel cell vehicles) or mobile energy sources for laptops and cell phones costs are very important (Kakaç *et al.* 2007). The cost may be even the deciding parameter. The real efficiency of fuel cell reaches even 80% (Hoogers 2003, O'Hayre *et al*. 2005, Redey 1973, Stolten 2010), because the FCs transforms the chemical fuel into electricity without intermediate stages. Moreover, FCs have many other advantages (Redey 1973, Hoogers 2003, O'Hayre *et al.* 2005):

- the maintenance of FCs is simple since there are few moving parts in the system,
- FCs can eliminate pollution caused by burning fossil fuels (considering only the process of energy production); for fuel cells fuelled by hydrogen, the only by-product at point of use is water, and for hydrazine FCs is additionally the nitrogen,
- low temperature FCs (like PEMFC or DMFC) have low heat transmission which makes them ideal for military applications,
- most FCs operate silently, compared to internal combustion engines (they are therefore ideally suited for hospitals),
- operating times of FCs are much longer than batteries, since doubling the operating time needs only doubling the amount of fuel and not the doubling of the capacity of the unit itself.

Fuel cells are powered mainly by hydrogen, methanol or hydrazine (Hoogers 2003, O'Hayre *et al.* 2005, Stolten 2010). However, problems with storage of hydrogen are the reason for the search of new fuels for FCs, e.g. crude oil or petroleum derivatives (Włodarczyk and Włodarczyk 2013, 2017c, 2017d) or biofuels (Włodarczyk and Włodarczyk 2016a, 2016b, 2017b, Włodarczyk *et al.* 2017a). The search of new catalysts for electrodes is also very important to obtain high current density of fuel cells and to lower costs of electrodes produc-

tion. However, first we must need to evaluate basic possibility of electrooxidation new fuel with reference catalyst – Pt (Bockris and Reddy 2000). Vegetable oil is an alternative fuel for Diesel engines and for heating oil burners. One of the vegetable oils is canola oil.

Canola seed oil is often used as additive for biodiesel fuel. Biodiesel is most commonly used as a blend with petroleum diesel fuel. Almost all the manufacturers of diesel vehicles and engines have approved the use of B5 (a blend containing 5% biodiesel and 95% petroleum diesel), and some approve the use of blends up to B20 (20% biodiesel and 80% petroleum diesel) or higher up to 100% biodiesel – B100 (Peterson *et al.* 1983, Van Gerpen 2005, Sheehan *et al.* 1998). Canola oil is difficult to use as fuel for diesel engines, because the viscosity of canola oil is 15-20 times greater than the kinetic viscosity of the diesel fuel. Moreover it cannot also be used below 10°C, because it changes consistency to similar margarine (Recep *et al.* 2001, Agarwal 2007, Bocheński and Bocheńska 2008). Canola oil has also lower energy content compared the diesel fuel (about 13%), but it is an environmentally friendly alternative to using diesel fuel. There has been an increasing demand for this type of fuel since it is ecologically safe for application in sensitive areas such as waterways, forestry or agriculture. This type of product is biodegradable, i.e. it can be broken down naturally (Nag *et al*. 1995, Ma and Hanna 1999).

Previous research of canola oil electrooxidation has shown that is possible of electricity production from canola oil in alkaline electrolyte (Włodarczyk and Włodarczyk 2016a). The paper presents the electrooxidation of canola oil with Pt catalyst in acid electrolyte (H_2SO_4) in various temperatures, and various concentration of canola oil. As with previous studies, Syntanol DS-10 was used as a detergent. Syntanol DS-10 is a mixture of primary oxygen-ethylene-glycol ethers of fatty alcohol of C_{10}-C_{18} fraction, and is characterized by high superficial activity, emulgation, dispersion, solubilization capabilities (Paraska and Karvan 2010, Sakharov *et al.* 1975; Survila *et al.* 2005). After electrooxidation of emulsion Syntanol DS-10 can be degraded e.g. by bacteria (Ignatov *et al.* 1995, Kravchenko *et al.* 1994).

MATERIAL AND METHODS

Due to adding fuel (canola oil) to the electrolyte during measurements, using the detergent is necessary. Moreover, canola oil does not conduct the electric current. To add canola oil to electrolyte (and cause the conduction) an intermediate agent (Syntanol DS-10) to solve canola oil in water was used. Investigated emulsion was obtained by mixing using a mechanical stirrer with the speed of about 1200 rpm. Proportion of water-detergent-oil was equal 2:1:1. Emulsion stabilization time was about 8 hours. Measurements were done by the method of

polarizing curves of electrooxidation of canola oil emulsion on a smooth platinum electrode in acid electrolyte (H_2SO_4).

In first step was carried of measurement the stationary potential of the working electrode. Measurements were done in glass vessel (reactor). Platinum was used as a catalyst of working electrode (Bockris and Reddy 2000) and saturated calomel electrode (SCE) was used as a reference electrode (Holtzer and Staronka 2000). Researches of electrooxidation of the emulsion based on canola oil in acid electrolyte (aqueous solution of H_2SO_4), for various concentrations of canola oil and detergent at various temperatures (293-333K). Concentration of canola oil (during measurement of electrooxidation) was equal 0.005%; 0.010%; 0.030% and 0.060% of working reactor volume. Electrooxidation were performed with potentiostat AMEL System 5000. The potentiostat was connected with computer to data recording. The scheme (Figure 1) shows the research position for measurements of canola oil electrooxidation.

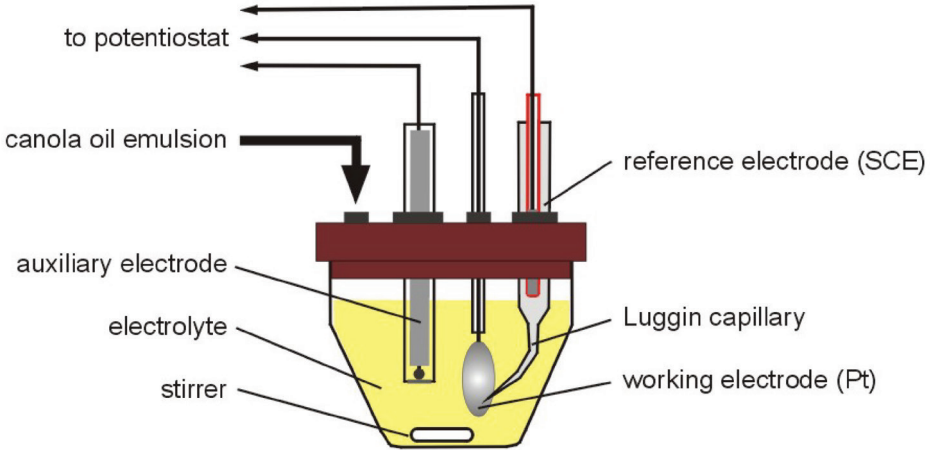

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Figure 1. Scheme of glass cell (reactor) for canola oil electrooxidation

RESULTS

In first step was carried measurements on electrooxidation of Syntanol DS-10 in acid electrolyte (aqueous solution of H_2SO_4), for various concentrations detergent at temperatures 293-333K. Next, the measurements were taken on electrooxidation of canola oil emulsion in aqueous solution of H_2SO_4 electrolytes, for various concentrations of the detergent at temperatures of 293-333K. The comparison of these two processes (electrooxidation of Syntanol DS-10 and

canola oil emulsion) allowed to determine whether the electricity is generated form the electrooxidation of the canola oil, or just from the detergent (in this case Syntanol DS-10). Figures 2-6 show electrooxidation of canola oil emulsion in H_2SO_4 at the temperature of 293-333K.

To ascertain that the emulsion and not the detergent was electrooxidated, measurements of electrooxidation process run in the scope of kinetics, but the potential on electrode is low and establishes in a long period of time. The highest results of potential were obtained at the temperature of 323K. With the increase in temperature to 333K first electrooxidation of Syntanol DS-10 takes place, and only then of canola oil emulsion.

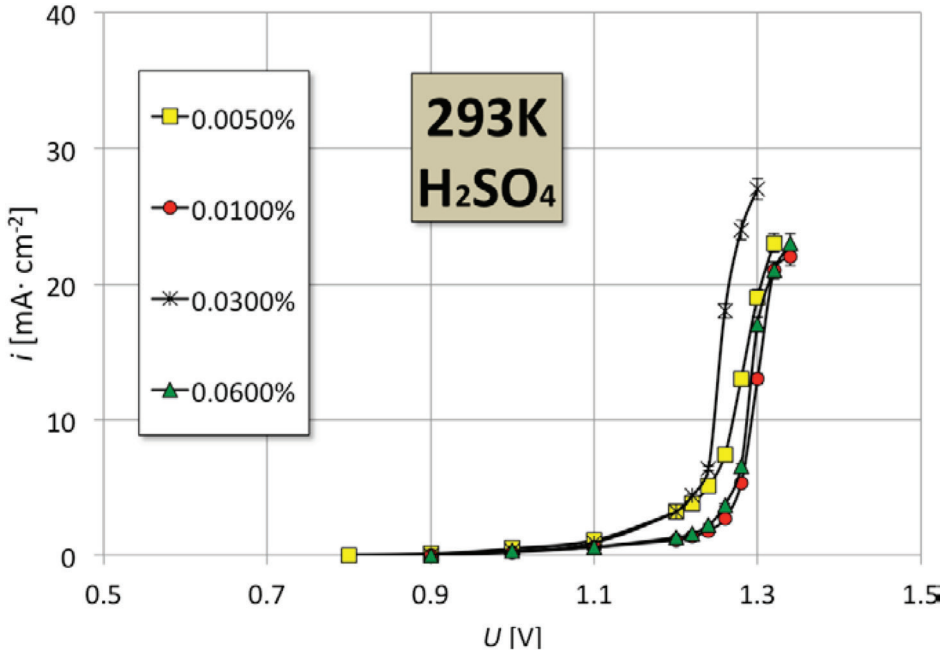

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Figure 2. Polarization curves of canola oil emulsion electrooxidation in 0.1n concentration of electrolyte H_2SO_4 at temperature 293K; Concentration of canola oil was equal 0.005%; 0.010%; 0.030% and 0.060% (of working reactor volume)

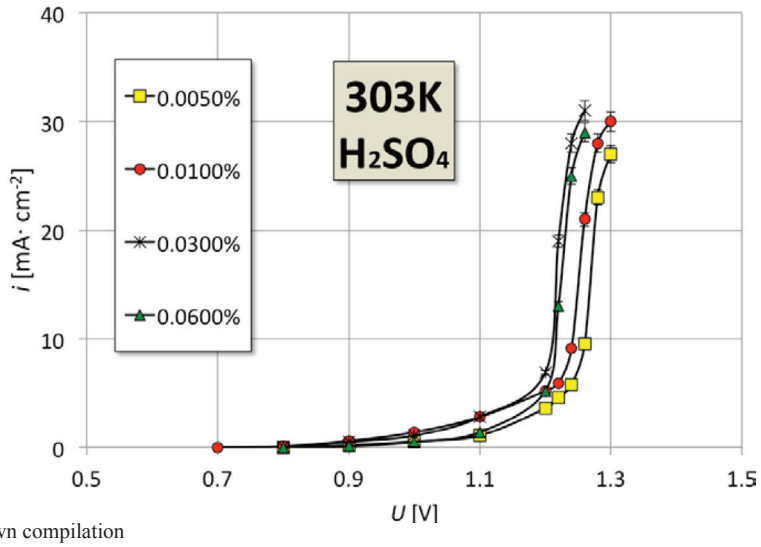

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Figure 3. Polarization curves of canola oil emulsion electrooxidation in 0.1n concentration of electrolyte H_2SO_4 at temperature 303K; Concentration of canola oil was equal 0.005%; 0.010%; 0.030% and 0.060% (of working reactor volume)

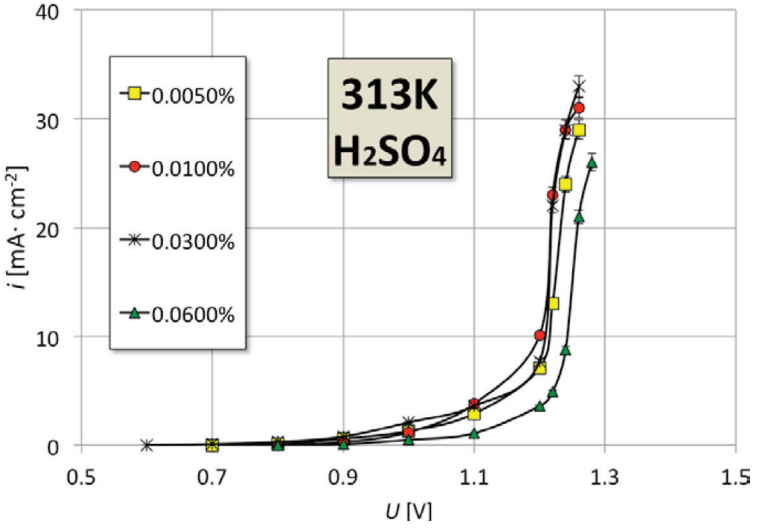

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Figure 4. Polarization curves of canola oil emulsion electrooxidation in 0.1n concentration of electrolyte H_2SO_4 at temperature 313K; Concentration of canola oil was equal 0.005%; 0.010%; 0.030% and 0.060% (of working reactor volume)

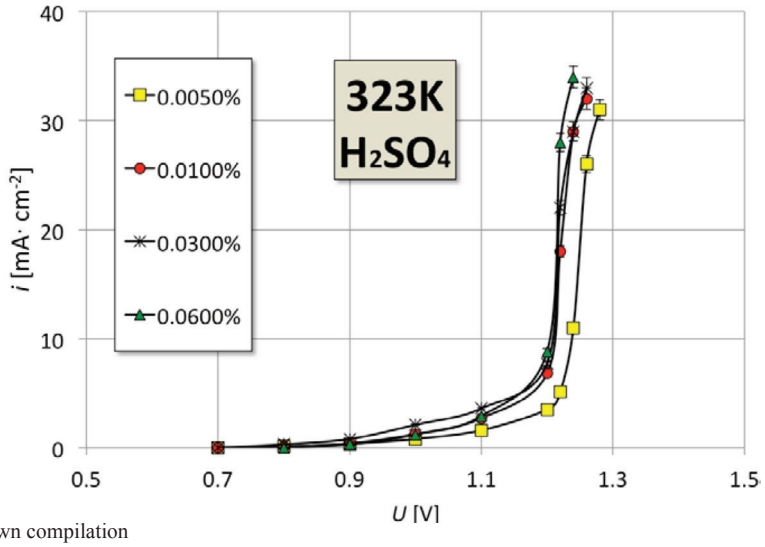

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Figure 5. Polarization curves of canola oil emulsion electrooxidation in 0.1n concentration of electrolyte H_2SO_4 at temperature 323K; Concentration of canola oil was equal 0.005%; 0.010%; 0.030% and 0.060% (of working reactor volume)

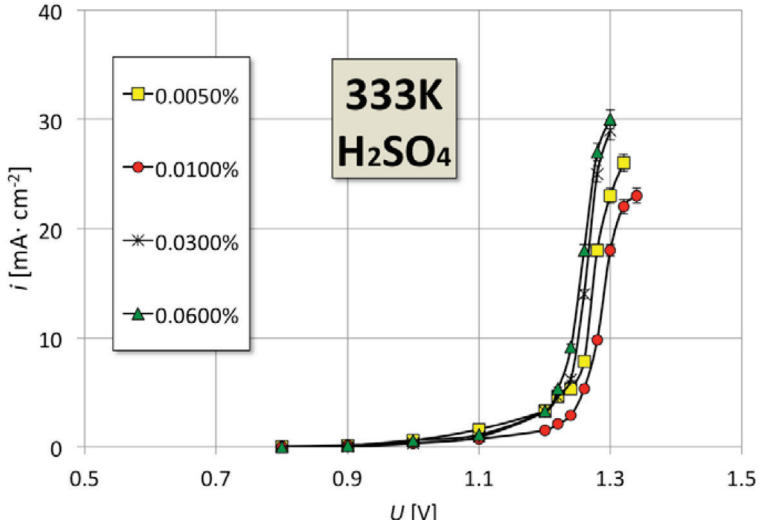

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Figure 6. Polarization curves of canola oil emulsion electrooxidation in 0.1n concentration of electrolyte H_2SO_4 at temperature 333K; Concentration of canola oil was equal 0.005%; 0.010%; 0.030% and 0.060%(of working reactor volume)

CONCLUSIONS

First was measurement the stationary potential of working electrode (Pt). This potential was establishing in time of about 29 minutes and was badly reproducible. Stationary, current-free real potential is included in potentials range from 0.58-1.11 V. The comparison of electrooxidation of Syntanol DS-10 and canola oil emulsion allowed to note that during electrooxidation of the canola oil emulsion is obtained a higher current density value than during the electrooxidation of only the detergent. In any case (for all concentration of canola oil and for all temperatures), the process of electrooxidation of canola oil emulsion occurred. A current density of half-cell of about 2.3-4.4 mA/cm^2 was obtained for all concentrations of canola seed oil. The current density for emulsion is 0.5-3.0 mA/cm^2 higher than current density for detergent for all concentration of oil and detergent. This situation occurred for temperatures 293-323 K. With the increase in temperature to 333K the first electrooxidation of Syntanol DS-10 took place, and only then of canola oil. So, it is necessary to conduct an electrooxidation process below the temperature of 333K to obtain high current density of cell. During electrooxidation of canola oil emulsion, at the temperature 293 K, was obtained current density in the range 2.3-4.4 mA/cm^2. At the temperature 303 K was obtained current density in the range 4.1-5.7 mA/cm^2. At the temperature 313 K was obtained current density in the range 5.2-7.2 mA/cm^2. And at the temperature 333 K was obtained current density in the range 3.4-5.1 mA/cm^2. The highest results of the current density were obtained at temperature of 323K (7.4-8.0 mA from 1 cm^2 of smooth surface platinum electrode). It has been demonstrated that using the detergent Syntanol DS-10 to prepare the emulsion of canola oil allows for the electrooxidation of canola oil in acid electrolyte, and thus a possibility of direct conversion of canola oil into electrical energy. So, it is possible using canola oil as fuel for fuel cells. Future research will be targeted the construction of a test fuel cell powering with canola oil emulsion.

REFERENCES

Agarwal, A.K. (2007). *Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines*. Progress in Energy and Combustion Science, 33: 233–271.

Bocheński, C., Bocheńska, A. (2008). *Rape oil as a fuel for diesel engines*. Czasopismo Techniczne, Wydawnictwo Politechniki Krakowskiej, 8M: 133-142.

Bockris, J.O.M., Reddy, A.K.N. (2000). *Modern electrochemistry*. New York: Kulwer Academic/Plenum Publishers.

Holtzer, M., Staronka, A. (2000). *Chemia fizyczna. Wprowadzenie*. Kraków: Wydawnictwo AGH.

Hoogers, G. (2003). *Fuel cell technology handbook*. Boca Raton: CRC Press.

Ignatov, O.V., Shalunova, Iu.V., Panchenko, L.V., Turkovskaia, O.V., Ptichkina, N.M. (1995). Degradation of Syntanol DS-10 by bacteria immobilized in polysaccharide gels (article in Russian), Prikl Biokhim Mikrobiol., 31 (2): 220-223.

Kakaç, S., Pramuanjaroenkij, A., Vasilev, L. (Eds.). (2007). *Mini-micro fuel cells: Fundamentals and applications*. New York: Springer-Verlag.

Kravchenko, A.V., Rudnitskii, A.G., Nesterenko, A.F., Kublanovskii, V.S. (1994). Degradation of Syntanol DS-10 promoted by energy transfer reactions, Ukrainian Chemistry Journal C/C of Ukrainskii Khimicheskii Zhurnal, 60 (11): 11-13.

Larminie, J., Dicks, A. (2003). *Fuel cell system explained, 2nd Edition*. John Wiley & Sons Ltd.

Ma, F., Hanna, M.A. (1999). Biodiesel production: a review, Bioresource Technology, 70 (1): 1-15.

Nag, A., Bhattacharya, S., De, K.B. (1995). New utilization of vegetable oils, J. Am. Oil Chem. Soc., 72(12): 1591-1593.

Nowicki, J., Zięcina, K. (1989). *Samoloty kosmiczne*. Wydawnictwa Naukowo-Techniczne.

O'Hayre, R., Cha, S.W., Colella, W., Prinz, F.B. (2005). *Fuel cell fundamentals*. Hoboken: John Wiley & Sons.

Paraska, O., Karvan, S. (2010). *Mathematical modelling in scientific researches of chemical technology processes*. Technical Transactions. Mechanics, Cracow University of Technology Press, 8 (107): 203-210.

Peterson, C.L., Wagner, G.L., Auld, D.L. (1983). *Vegetable oil substitutes for diesel fuel*. Transactions of the ASAE, 26 (2): 322-327.

Recep, A., Selim, C., Huseyin, S. (2001*). The potential of using vegetable oil as fuel for diesel engine*. Energy Conversion & Management, 40: 529-538.

Redey, L. (1973). *Ogniwa paliwowe*. Warszawa: Wydawnictwa Naukowo-Techniczne.

Sakharov, Iu.I., Rastiannikov, E.G., Verbitskaia, G.M., Tarasova, L.N. (1975). Washability of syntanol DS-10 from kitchen utensils (article in Russian), Vopr Pitan., 4: 75-7.

Sheehan, J., Camobreco, V., Duffield, J., Graboski, M., Shapouri, H. (1998). *An overview of biodiesel and petroleum diesel life cycles*. National Renewable Energy Laboratory, Prepared for U.S. Department of Energy's Office of Fuels Development and U.S. Department of Agriculture's Office of Energy.

Stolten, D. (2010). *Hydrogen and fuel cells. Fundamentals, technologies and applications*. Weinheim: Wiley-VCH.

Survila, A., Mockus, Z., Kanapeckaitė, S., Samulevičienė, M. (2005). *Effect of syntanol DS-10 and halides on tin(II) reduction kinetics*. Electrochimica Acta, 50 (14): 2879-2885. https://doi.org/10.1016/j.electacta.2004.11.034.

Van Gerpen, J. (2005). *Biodiesel processing and production*. Fuel Processing Technology, 86 (10):1097-1107.

Włodarczyk, P.P., Włodarczyk, B. (2013). *Powering fuel cell with crude oil*. Journal of Power Technologies, 93 (5): 394-396.

Włodarczyk, P.P., Włodarczyk B. (2016a). *Canola oil electrooxidation in an aqueous solution of KOH – Possibility of alkaline fuel cell powering with canola oil*. Journal of Power Technologies, 96 (6).

Włodarczyk, P.P., Włodarczyk, B., (2016b). *Electrooxidation of diesel fuel in alkaline electrolyte*. Infrastructure and Ecology of Rural Areas, 4 (1): 1071–1080. DOI: http://dx.medra.org/10.14597/infraeco.2016.4.1.078.

Włodarczyk, P.P., Włodarczyk, B., Kalinichenko, A. (2017a). *Possibility of direct electricity production from waste canola oil*. E3S Web of Conferences, 19, 01019. DOI: 10.1051/e3sconf/20171901019.

Włodarczyk, P.P., Włodarczyk, B. (2017b). *Electrooxidation of coconut oil in alkaline electrolyte*. Journal of Ecological Engineering, 18 (5): 173-179. DOI: 10.12911/22998993/74623.

Włodarczyk, P.P., Włodarczyk, B. (2017c). *Elektroutlenianie odpadowego syntetycznego oleju silnikowego w wodnym roztworze H_2SO_4*. Inżynieria Ekologiczna, 18 (1): 65-70. DOI: 10.12912/23920629/66985.

Włodarczyk, P.P., Włodarczyk, B. (2017d). *Electricity production from waste engine oil from agricultural machinery*. Infrastructure And Ecology Of Ruras Areas, 4 (2): 1609-1618. DOI: http://dx.medra.org/10.14597/infraeco.2017.4.2.121.

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