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THE APPLICATION OF MICROWAVE IRRADIATION IN THE PRODUCTION OF VEGETABLE OIL-BASED FUELS

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Abstract: The importance of the research activities in biofuels is based on both the Hungarian Renewable Energy Action Plan and Europe 2020 which emphasize the support for the intelligent and sustainable development. At the same time it is important research, development and innovation performance – which are moderate at the present time (under the EU average) – because these are marked among the main targets of the Innovation Union. In this paper the direct objective of research programme is to examine the bioenergetic utilization of the microwave irradiation and on the other hand to ensure the safety of the energy supply. Based on the previous experiences the microwave energy can intensify chemical reaction. Preliminary research experience has showed that the microwave assisted transesterification process (transesterification with methanol and NaOH catalyst) reduced the reaction time and the energy demand. The microwave assisted biodiesel production was carried out under various parameters operational, procedure and process parameters. The results of the research proved that the reaction time of the microwave irradiated transesterification was decreased significantly compared to the conventional transesterification process. However more research is needed to study and determine the composition of the mixture and the dielectric properties of the components in order to optimize the energy demands.
Keywords: biofuels, biodiesel, microwave irradiation

1. INTRODUCTION

Nowadays sustainable development and sustainable survival are key dominant phenomena. For this reason the European Union (EU) focuses on the green environment so supports production and utilization of biofuel to decrease the emission. In recent years the energy anomalies and their economic consequences draw attention to the fact that it is need to decrease the level of the energy dependency from other countries. One possible way of reducing energy dependence is to develop the energy production technologies. Therefore it is necessary both from energy saving and environmental protection aspects more cost effective method of biofuel production. The microwave technology can be innovative in terms of production time and energy efficiency. Reducing the energy demand of the technology process is very important to achieve the overall cost reduction of the production.

The utility of the microwave technology has been investigated in agricultural and food industry processes for decades and its efficiency is demonstrated. In the last decade more and more research groups have been dealing with its utilization in environment protection techniques: for example in disposal of contamination or in energetic utilization of waste. It is justified to perform some experiments to demonstrate the theoretical foundations of interaction of the microwave irradiation with different materials. The interaction of different materials – among them vegetable oils as well – with electro-magnetized energy (especially microwave energy) was examined by [Ponne – Bartels, 1995.]. It has been found that the dissipation of the microwave energy, the indicators of the energy utilization of the process and the reactions in the materials are influenced by physical, heat and dielectric properties of the materials.

Recently the application of microwave for energy purposes comes into view in the microwave-assisted biodiesel production. Among numerous publications and studies [Schuchardt et al., 1998.]

have optimized rate of the ideal alcohol-vegetable oil-catalyst based on the yield indicators. The microwave irradiation technique is an energy efficient method of expediting the chemical reactions [Lidström et al., 2001.]. In many cases the transformation efficiency of the organic chemical synthesis can be improved by microwave irradiation and the properties of the final product and by-products and also the utilization characteristics may be improved. Furthermore, the use of solvents and catalysts can be avoided or minimized in some cases [De La Hoz et al., 2002.]. Several groups have made technological experiments to determine the circumstances of the microwave-assisted transesterification of vegetable oils empirically. [Leadbeater – Stencel, 2006.] and [Al Zuhar, 2010.] investigated the opportunities and challenges of biodiesel production. While [Orliac – Silvestre, 2007.] studied how can be increased level of transesterifacation and they achieved higher yields and shorter reaction time by a combination of a greater amount of catalyst and microwave energy compared to conventional transesterification. In such way the biodiesel has a remarkable potential to be a part of a sustainable energy mix in the future, especially in the transportation sector [Demirbas et al., 2007.].

Later [Shakinaz et al., 2010.] made some tests by using non-edible vegetable oil (Jatropha) and waste vegetable oil, and [Ozturk et al., 2010.] made some tests by using oil of high linoleic acid content (obtained from corn germ). They have demonstrated that the use of microwave irradiation accelerates certain chemical reactions by the selective absorption of microwaves and thermal effects on the molecular level. [Manco et al., 2011.] produced biodiesel from sunflower oil. Different types of pebbles were applied to perform the experiments in the presence of methanol and KOH. The obtained results showed that using microwave irradiation and carborundum significantly decreased the reaction time.

There are few studies for the beneficial effects of microwave energy manipulation for biogas production technologies. For example in terms of sewage sludge the microwave pre-treatment improves the solubility properties of organic substances and also makes more accessible these organic substances to the decomposing microorganisms for the biogas fermentation. In the anaerobic fermentation processes these effects are preferred for both the biogas yield indicators and the rate of increase of biogas production [Kovács et al., 2012.].

All researchers have mentioned the local temperature rise and acceleration effect as the special influences of microwave irradiation. In their review paper [Motasemi – Ani, 2012.] report on the research and development of microwave assisted biodiesel production in the last ten years. And they have made simplified energy recovery calculations assuming the utilization of biodiesel as fuel so concluded sustainability of the production and utilization system.

Based on the previous results the main objective of our research work is the investigation of transesterification process with some vegetable oil (being available in Hungary and can be used as fuel in the EU): optimizing operational parameters (which depend on the raw material) based on energy indicators as well as correlation analysis of the quality parameters and dielectric parameters of the biodiesel. In the first phase of this research project it should be designed the experimental apparatus carrying out research tasks, and then should be created the experimental method and the energy measurement/calculation methods, furthermore to perform the transesterification process for testing and optimization features for some vegetable oils.

2. BIODIESEL PRODUCTION BY MICROWAVE IRRADIATION

The main objective of the technological experiment was to determine the differences/similarities of the microwave-assisted transesterization of vegetable oils (sunflower, rapeseed oils that can be used as fuel in internal combustion engine) with microwave energy compared to conventional transesterification. As the result of microwave-assisted transesterification it can be calculated the dissipated performance from the dielectric properties of the biodiesel and the energy indicators can be determined by the basic physical, chemical, combustion technology and quality parameters of the biodiesel.

The indirect objective of the research is to contribute to the promotion of sustainable energetics by fulfilling the environmental sustainability criteria of 2009/208/EC RED (Renewable Energy Directives) to the biofuels.

2.1. Experimental apparatus

The experimental apparatus for our research is available in the Thermodynamics and Fluid Mechanics Laboratory of the Institute of Process Engineering at University of Szeged, Faculty of Engineering. The microwave-assisted transesterification with methanol was done in a modified household microwave oven in a flow system. The condensation of vapor (due to the heat generated in the transesterification) was carried out in a closed system buffer tank via laboratory cooling coil under laboratory vent cabin.

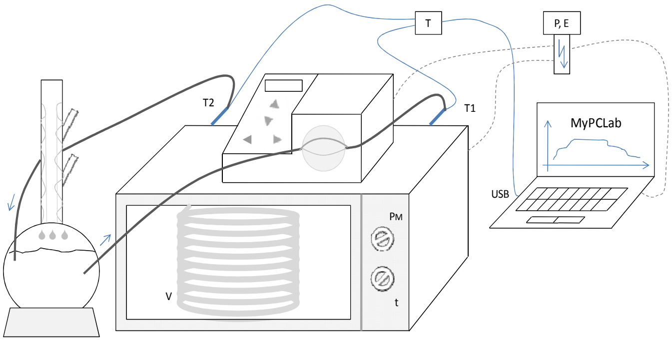

Figure 1 .Microwave system

In order to implement the microwave treatment field the household microwave oven has been modified that is equipped with PTFE spiral (pipe size is 8/10 mm diameter, 15 threads) and temperature sensors and a measurement and data collecting computer system with the myPCLab software which can able to measure and record the input and output temperature values of the dielectric, and a peristaltic pump for continuous material flow. The useful volume is 405 cm^3 which is calculated by the pipe size and the threads. Figure 1 illustrates the schematic layout of the apparatus. The microwave device works at 2450 MHz (at an outdoor wavelength of 12.24 cm) and generates 700 W maximum magnetron power in the cavity resonator which has 0.25 m depth and 0.18 m height.

2.2. The process parameters of microwave-assisted transesterification

In Hungary the most important vegetable oils are sunflower oil and rapessed oil they can be used as fuel in the internal combustion engine. In the course of the preliminary experiments, the transesterification of these vegetable oils were made by methanol and efficient NaOH catalyst. The experimental mixture (vegetable oil, methanol and catalyst) is a multi-component mixture (dielectric) that contains both polar and ionic molecules. Methanol belongs to the materials which are well-absorbing the micro waves. This is due to the rearrangement of the hydroxyl groups (OH^-) in the changing polarity, high frequency electromagnetic fields so the kinetic energy results intense local heat generation. The high energy density of the microwave treatment furthermore the different dielectric properties of the components in the mixture cause selective heating. So the temperature-dependent reactions will happen faster.

Dielectric and thermal properties of the material are affected by the different fatty acid composition of the different kinds of oils. Table 1 contains the composition of the vegetable oils and the quantitative rate of the various fatty acids which have different carbon numbers. The specific heat capacity values of the experimental mixture can be calculated from the mass concentrations and thermal properties of the components according to [Zong et al., 2010.]:

Table 1. Composition of the vegetable oils

Fatty acids	Sunflower oil	Rapeseed oil
Palmitic acid (C 16:0)	6.64%	5.19%
Stearic aci (C 18:0)	3.46%	1.68%
Oleic acid (C 18:1)	30.46%	60.89%
Linolic acid (C 18:2)	57.72%	21.37%
Linolenic acid (C 18:3)	0.08%	8.13%
Arachin acid (C 20:0)	0.27%	0.48%
Gadolic acid (C 20:1)	0.15%	1.10%
Behenic acid (C 22:1)	0.76%	0.24%

- for mixture of sunflower oil:methanol:NaOH $c_P=2.415$ kJ·kg^{-1}·K^{-1}
- for mixture of rapeseed oil:methanol:NaOH $c_P=2.233$ kJ·kg^{-1}·K^{-1}

When determining the operational and process parameters of the microwave-assisted transesterification we should take into account the different dielectric properties of the mixture components (vegetable oil, methanol, NaOH) because the dielectric behaviour of the mixture depends strongly on the structure of the molecules besides the temperature. The process parameters of the procedure are determined by the preliminary experiments and the literature:

☐ vegetable oil ratio of the mixture: 82%
☐ methanol ratio of the mixture: 18%
☐ amount of the catalyst: 0.5% of the vegetable oil mass
☐ microwave irradiation power: 418.1 W
☐ (from the magnetron power and the ratio of the irradiation/non-radiation time periods)
☐ reaction times (taking into account the outlet temperature below the boiling point of methanol): 300 and 360 sec
☐ character of the process: continuous material flow

3. EXPERIMENTAL RESULTS

The dielectric properties of the tested vegetable oil, the dissipated power, invested energy, the total energy demand of the microwave-assisted transesterification and its efficiency and effectiveness can be determined from the T_{in} and T_{out} temperatures recorded by the myPCLab software and from the temperature profiles and from the geometrical parameters the cavity resonator and the thermal properties of the dielectric. The comparison is always based on the conventional transesterification. Since there is no phase shift in the cavity resonator, therefore ε' the real part of the dielectric constant (permittivity) can not feed back to the dissipated power. The parameter ε'' being the imaginary part of the dielectric constant (dielectric absorption factor) is the indicator of the microwave energy turning into heat. In the case of known material composition the heat energy can be calculated from the specific heat capacity value, the mass flow rate and the temperature rise of the treated mixture (by classical caloric method) and this thermal energy is the same as the dissipated microwave power in the material. Accordingly, the microwave power absorbed in the dielectric material can be expressed in terms of thermal characteristics (1) and in terms of electrical and dielectric parameters (2):

$$P_{dissipated} = c_p \cdot m \cdot \dot{T} \quad [\mathrm{W}] \tag{1}$$

$$P_{dissipated} = 2 \cdot \pi \cdot \varepsilon_0 \cdot f \cdot E_{RMS}^2 \cdot \varepsilon''_{(Tk)} \quad [\mathrm{W \cdot m^{-3}}] \tag{2}$$

ε″ can be determined from equations (1) and (2), and by substituting ε″ back into one of the equations we get the dissipated power. The calculation is done by using the following quantities and partial correlations:

- c_p – the average specific heat of the mixture [$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$], m – the weight of the mixture [kg]
- $\dot{T} = \dfrac{dT_k}{dt}$ [$\mathrm{K \cdot s^{-1}}$] (3)
- ε_0 – electric permittivity [$\mathrm{A \cdot s \cdot V^{-1} \cdot m^{-1}}$], f – frequency [$\mathrm{s^{-1}}$]

E_{RMS} [$\mathrm{V \cdot m^{-1}}$] electric field in equation (2) can be calculated from the power side impedance, the average magnetron power and the geometric dimensions of the cavity resonator:

$$E_{RMS}^2 = \frac{4 \cdot P_{magnetron} \cdot Z_{power\,side}}{a \cdot b}, \tag{4}$$

where: $P_{magnetron}$ – magnetron power [W], $Z_{power\,side}$ – power side impedance [$\mathrm{V \cdot A^{-1}}$], a – depth of the power side [m], b – height of the power side [m]

The power side impedance can be determined by:

$$Z_{powerside} = \frac{Z_0}{\sqrt{1-\left(\dfrac{\lambda_0}{2 \cdot a}\right)^2}}, \tag{5}$$

- Z_0 – wave impedance [$\mathrm{V \cdot A^{-1}}$] according to $Z_0 = \sqrt{\dfrac{\mu_0}{\varepsilon_0}}$ (6)
- λ_0 – wavelength [m] according to $\lambda_0 = \dfrac{c}{f}$ (7)

Based on the above the dielectric feature of the given mixture can be calculated by equations (1) and (2), and can be determined continuously during the experiment as the function of the temperature:

$$\varepsilon''=\frac{c_p \cdot m \cdot \dot{T}}{2 \cdot \pi \cdot \varepsilon_0 \cdot f \cdot E_{RMS}^2} \tag{8}$$

The dielectric constant shows how the electric field can affect to the given medium (dielectrics). The dielectric constant of the tested multi-component materials is in non-linear relationship with the temperature. Frequency, temperature and composition of the dielectric material affect together the dielectric properties. The mixture of the components and their compositional ratios influence the value of ε".

It can be observed that in the case of sunflower oil when the reaction time is 300 s the imaginary part (ε") of the complex dielectric constant reaches the maximum value (2.93) at 33.7 °C accordingly the specific absorption rate is 1.56 $W \cdot g^{-1}$. While in the case of rapeseed oil the total maximum (1.86) of ε" is at 32.3 °C when the specific absorption rate is 1.07 $W \cdot g^{-1}$. The vegetable oils have a good absorption ability which increases the reaction energy efficiency and makes the reaction time shorter.

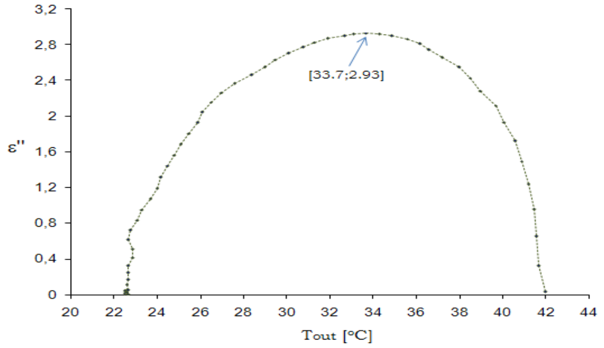

Figure 2. ε" as the function of the output temperature during the microwave-assisted transesterification of sunflower oil

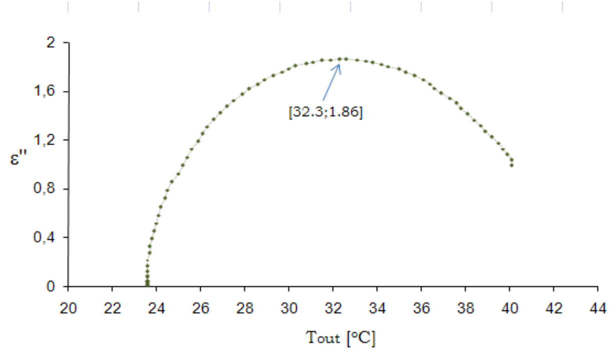

Figure 3. ε" as the function of the output temperature during the microwave-assisted transesterification of rapeseed oil

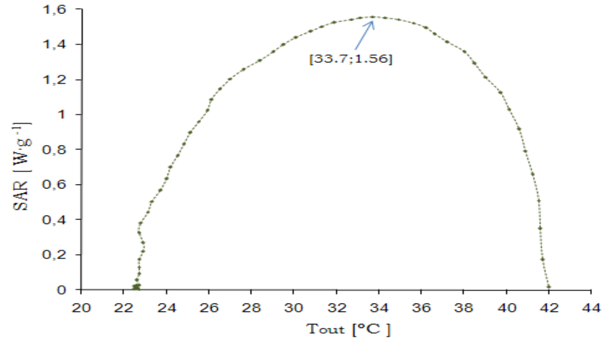

Figure 4. Specific Absorption Rate as the function of the output temperature during the microwave-assisted transesterification of sunflower oil

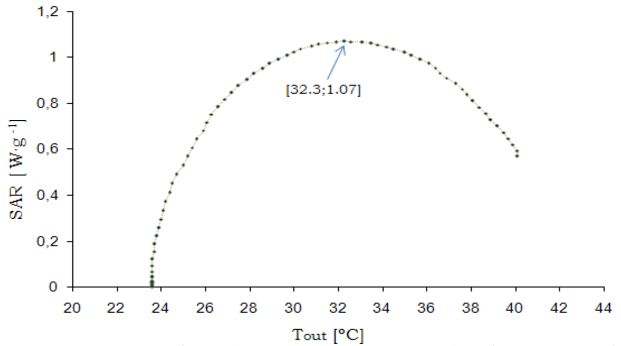

Figure 5. Specific Absorption Rate as the function of the output temperature during the microwave-assisted transesterification of rapeseed oil

During the microwave-assisted transesterification, it always has to be taken into account that the dielectric constant of the given multicomponent material – based on the so-called multi-permittivity principle – iss between the minimum and maximum dielectric constants of the components with different dielectric features. In case of increasing temperature dielectric (vegetable oil and methanol) the dielectric factor decreases after the maximum value that is the material absorbs less microwave power. Accordingly there forms a self-regulating and self-limiting process that can be modeled absolutely.

Table 2 contains the measured an/or calculated results of microwave-assisted transesterification experiments in case of sunflower and rapeseed oil experiments, in particular those characteristics that affect the efficiency of the transesterification.

Table 2. The main parameters of the microwave-assisted transesterification

Parameters	Microwave-assisted transesterification	
	sunflower oil	rapeseed oil
average magnetron power [W]	418.1	418.1
yield [%]	93.7-96.8	94.5-97.5
energy demand [J/ml biodiesel]	390-403	387-400
Specific Absorption Rate (SAR) [W/g mixture]	<1.56	<1.07
process efficiency	high	
method	continuous	

During the technological improvements besides the cost- and energy efficiency it is required that the quality of the biodiesel fuel should not deteriorate. To control the latter during the microwave assisted procedure it is desirable to determine the main physical, chemical and combustional attributes (kinematic/dynamic viscosity, open cup flash point, I-Br number, Low Heating Value) of biodiesel fuels.

4. CONCLUSIONS

Based on the results it can be concluded that the microwave-assisted transesterification of vegetable oils (sunflower oil, rapeseed oil) is an energy efficient and quick process so reduces the cost of the product. The conventional method of heating has long reaction time and high energy demand. According to the experimental results, the further direction of research task could be the investigation of the connections between the dielectric parameters and the quality parameters (viscosity etc.) and then it is necessary to elaborate a monitoring system to observe the dielectric parameters in-process and to develop an energetics model that can be treated mathematically so all the features and parameters which affect the energy operators should be taken into account.

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