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Effect of Ultrasound on Biodiesel Synthesis from Plant Oil

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Abstract: The recent studies have clearly shown that the continuous exploitation of fossil fuels has adverse effects on the environment, while reserves of oils are sufficient for about next fifty years. As the need for energy rises, so do the energy policies tend to develop and research the renewable energy sources including biodiesel. The goal of this research is to examine the ultrasound effect on biodiesel synthesis process and to optimize synthesis conditions, examining the effect of several parameters in production process and biodiesel quality. Biodiesel synthesis was processed out of unused sunflower oil and sunflower oil used in fast-food (waist oil). Particularly, the ultrasound effect on production process-transesterification reaction was examined. After synthesis, examination of density, viscosity, flash point and yield were done using suitable apparatus and methods. The study results proved that the most optimal temperature with the use of ultrasound is 60^{o}C, sonication time of 15 minutes and alcohol-oil molar ratio 3:1. Also, the results proved that using ultrasound during biodiesel synthesis, transesterification reaction can be processed on lower temperatures and still, biodiesel of good quality can be produced, contrary to conventional synthesis. Using the ultrasound generator for laboratory biodiesel synthesis largely shortens reaction time, increases rate of chemical reaction, decreases by-product amount, decreases alcohol amount, decreases waste water and, in the end, saves energy because the reaction is faster and takes less time at lower temperatures.

INTRODUCTION

In recent years, fatty acid methyl esters derived from vegetable oil, commonly known as biodiesel, have gained importance as alternate fuel for diesel engines. Due to closed carbon cycle, biodiesel does not contribute to global warming. An analysis of the life cycle of biodiesel shows that overall CO_2 emissions are reduced by 78% compared with petroleum-based diesel fuel(Gerpen*et al.,* 2005;Sheehan*et al.,*1998).

Biodiesel also has a relatively high flash point (150^{o}C), which makes it less volatile and safer to transport or handle than petroleum diesel(Zhang *et al.,* 2003). Biodiesel can be synthesized by chemical, enzymatic and microbial methods. Alkali based esterification is the most often applied approach(Ranganathn*etal.,*2008). However, there are some drawbacks such as problems in the recovery of glycerol, the need to remove the catalyst, the requirement to use oils without free fatty acids and high energy consumption. A high level of interest from industry initiated research concerning non-catalytic biodiesel synthesis from rapeseed oil in supercritical methanol, which has a conversion of 80% (350^{o}C, 45–65MPa, 240 s). Recently, the application of the ultrasound and hydrodynamic cavitation has also been reported to significantly intensify the synthesis of biodiesel (Gogate*et al.,* 2009; Kelkar*et al.,* 2008). It was demonstrated that hydrodynamic cavitation was about 40times more effective than acoustic methods (Gogate*et al.,* 2008; Wu *et al.,* 2007). The most important parameters that influence the transesterification reaction are: reaction temperature, ratio of alcohol to vegetable oil, type of acyldonor and acceptor, type and amount of catalyst, mixing intensity, quality (purity, free fatty acid content) of starting materials and water content(Nielsen *et al.,* 2008).

However, in this field, interest is increasingly moving in the direction of finding ways to minimize the cost of biodiesel production. The problem can be approached in two different ways: by finding a cheap source of raw material (Peterson, 1986; Alcantara*et al.,* 2000) or by intensifying the synthesis process by using novel reactors based on the use of enzymes, microwaves, supercritical fluids, ultrasound, or fluid energy (Kelkar*etal.*, 2008).

EXPERIMENTAL

Unused sunflower oil and used sunflower oil (used in fast food restaurants) were used for biodiesel production. KOH (p.a, Merck), methanol (p.a, Sigma Aldrich), ethanol (p.a, Sigma Aldrich), 2% phenolphthalein,ethanolic solution (Merck, p.a.) were used as received.

Used oil was purified by filtration to remove mechanical impurities (food residues). After that, oil was heated up to 105^{o}C during five to ten minutes, to remove possible water (Andričić, 2006).

Conventional synthesis was carried out at 65°C, with constant mixing (magnetic stirrer) during 45, 90 and 120 minutes. Methanol-oil molar ratio was 3:1. This ratio was chosen on the basis of experimental data from 12 synthesis samples (changing parameters: reaction time, catalyst type, oil type) (Čišija, 2013). Biodiesel synthesis using ultrasound generator (PHYWE, 800 kHz, 16 W/cm^2) was carried out on 25°C, 45°C and 60°C during 15,30 and 45 minutes, respectively. Methanol-oil molar ratios were 3:1, 6:1 and 9:1 (Gude*et al.,* 2013).

Product characterisation, after purification, was carried out by viscosity measurement (Ostwald), density measurement (pycnometer), flash point measurement (Marcuson), yield calculation (Vatrenjak-Velagić,1997).

RESULTS AND DISCUSSION

The goal of this research was to examine the ultrasound effect on the biodiesel synthesis process and to optimize synthesis conditions (shorten reaction time, to carry out reaction at lower temperatures, to get high quality biodiesel with economical benefit), contrary to conventional synthesis.

The results of biodiesel produced via conventional synthesis are given in Table 1. All reactions were carried out at 65°C during 45, 90 and 120 minutes with changing next parameters: reaction time, catalyst type, amount of catalyst and oil type. Alcohol-oil molar ratio for all reactions was 3:1 (Čišija, 2013).

Contrary to conventional synthesis, synthesis via ultrasound gave a product with much better characteristics (Lima *et al.,*2012),even at lower temperatures where conventional synthesis cannot be done, which is presented in this study.

Best quality biodiesel was produced from unused and used sunflower oil via conventional synthesis during 120 minutes with the magnetic stirrer.

Table1. Yield and biodiesel (conventional synthesis) characteristics, oil-alcohol molar ratio 3:1, temperature 65°C

Characteristic biodiesel produced out	Reaction time (min)	Unused sunflower oil	Used sunflower oil (kitchen)	Used sunflower oil (fast-food)
Density (g/mL)	45	0.8751	0.8749	0.684
	90	0.8898	0.8959	0.8801
	120	0.8983	0.8839	0.8698
Viscosity (mm^2/s) at 40°C	45	7.452	9.950	10.470
	90	7.112	9.807	9.870
	120	6.874	9.070	9.710
Flash point (°C)	45	48	44	51
	90	68	48	56
	120	97	51	62
Yield (%)	45	34.97	94.00	84.63
	90	93.00	95.41	89.23
	120	98.89	93.69	85.69

Reaction of transesterification (ultrasound synthesis) yields at 25°C were 90.56%, 93.08% and 95.75% with density 0.8691 g/mL, 0.8711 g/mL and 0.8771 g/mL. Viscosity value did not vary significantly: 6.11 mm^2/s, 5.93 mm^2/s and 5.71 mm^2/s. Also, flash point value did not vary significantly: 127°C, 129°C and 133°C.

Yields of reactions conducted at 45°C were 94.35%, 95.59% and 96.30%. Measured densities of biodiesel were 0.8832 g/mL, 0.8806 g/mL and 0.8873 g/mL. Viscosity values were 5.77mm^2/s, 5.89 mm^2/s and 5.92 mm^2/s. Flash point values were 131°C, 133°C and 135°C.

Yields of reactions conducted at 60°C were 97.50%, 98.57% and 96.40%. Measured densities of biodiesel were 0.8742 g/mL, 0.8790 g/mL and 0.8720 g/mL. Viscosity values were pretty much close: 5.63 mm^2/s, 5.54 mm^2/s and 5.57 mm^2/s. In this case, flash point values were 138°C, 149°C and 153°C.

Colluci and co-workers (Coluccî*et al.,* 2007), stated that yield of reaction which was administered by ultrasound mixing after 15 minutes at 25°C about 85%, at 40°C was around 87% and at 60°C yield was 88% (alcohol-oil molar ratio 3:1).

In the case of alcohol-oil molar ratio 6:1 at 25°C, yield was about 92%, at 40°C was 94.50%, and at 60°C yield was 97%. In the case of alcohol-oil molar ratio 9:1 at 60°C, after 15, 30 and 45 minutes, yields were just over 95%, with negligible variation.

Lima and co-workers(Lima *et al*., 2012) stated that at the 60°C (case with use of waste oil), alcohol-oil molar ratio 2.4:1, after 15 minutes yield was 98%, and after 30 and 45 minutes yields were very common99%. In the same conditions, but with conventional synthesis yield was lower, in fact, after 15 minutes was 88%, after 30 minutes was 92% and after 45 minutes was 96%.
Figure1 shows conventional reaction yield (Čišija, 2013) and ultrasound reaction yield depending onreaction time. It shows that ultrasound synthesis gives way much better yield in shorter time period contrary to conventional synthesis.

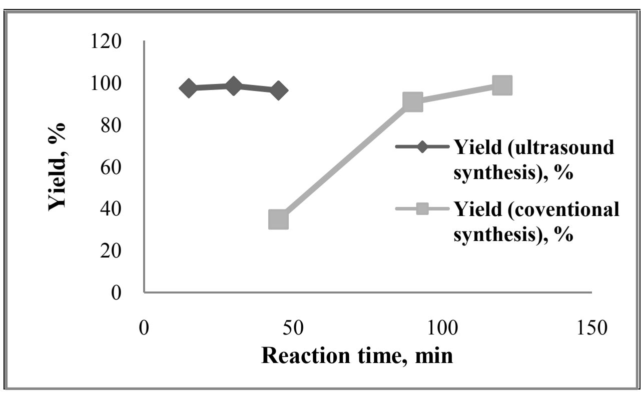

Figure1. Conventional reaction yield and ultrasound reaction yield depending on reaction time-used sunflower oil, alcohol-oil molar ratio 3:1, temperature 65°C

Figure 2.shows difference in viscosity values of biodiesel-conventional synthesis (Čišija,2013), and biodiesel-ultrasound synthesis.The flash point of a volatile material is the lowest temperature at which it can evaporate to form an ignitable mixture in air. At the flash point, the vapor may cease to burn when the ignition source is removed(Vatrenjak-Velagić, 1997).Biodiesel produced via ultrasound synthesis has much better values of viscosity: 5.49-5.72 mm^2/s. Biodiesel produced via conventional synthesis has higher values of viscosity: 9.71-10.47 mm^2/s(Čišija, 2013; Young *et al.,*1989).

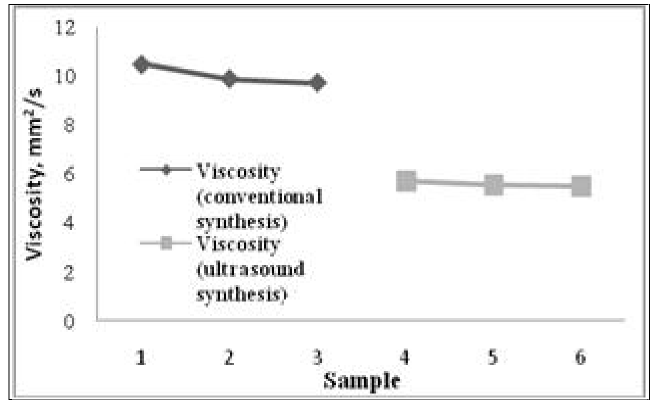

Figure 2. Dependence of biodiesel viscosity-ultrasound synthesis and conventional synthesis-used sunflower oil; alcohol-oil molar ratio 3:1

Flash point represents a major biodiesel quality factor. Biodiesels flash point is above 130°C to 180°C, which depends on raw material (Jurac, 2011). In this research, flash point values were all above 130°C (two exceptions-56°C and 120°C). The low flash point values were caused by impure chemicals (methanol) and bad mixing (magnetic stirrer)(Čišija, 2013).

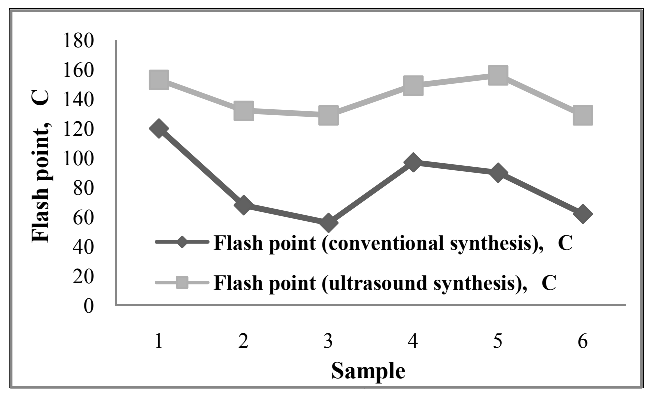

Figure 3. Dependence of biodiesel flash point, ultrasound synthesis, alcohol-oil molar ratio 9:1, and biodiesel flash point, conventional synthesis, alcohol-oil molar ratio 3:1- used sunflower oil

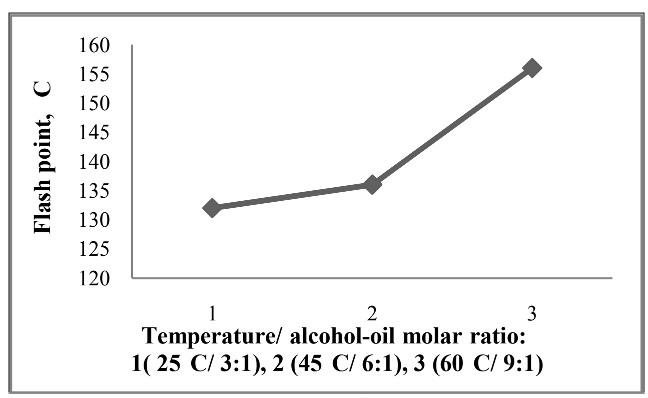

Figure 4. Flash point dependence (biodiesel produced via ultrasound synthesis) on alcohol-oil molar ratio and temperature

Comparing these results-Figures 1, 2, 3 and 4-one can conclude that using ultrasound gives much better quality of biodiesel contrary to conventional synthesis.

CONCLUSIONS

Synthesis conditions (temperature, reaction time, alcohol-oil molar ratio) have shown less effect on biodiesel produced out of unused sunflower oil, contrary to biodiesel produced out of used sunflower oil.

Considering the results, it is apparent that using the ultrasound generator, largely shortens reaction time and enhance yield, and improves biodiesel quality which, firstly, depends on raw material. Ultrasound field increasesrate of chemical reaction by intensifying mass transport and mixing. The outcome of ultrasound field is cavitation-bubble collapse-cavern which causes presence of local high temperatures, pressure and turbulence which, in the end results in speeding up chemical reaction. Also, better homogenization is a greatadvantage contrary to conventional synthesis.

Using the ultrasound generator for laboratory biodiesel synthesis largely shortens reaction time, increases rate of chemical reaction, decreases by-product amount, decreases alcohol amount, decreases waste water and, in the end, saves energy because reaction is faster and takes less time at lower temperatures.

REFERENCES

Alcantara R., Amores J., Canoira L., Fidalgo E., Franco M. J., Navarro A. (2000). Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. *Biomass and Bioenergy,* 18(6), 515-527.

Andričić B. (2006).*Vježbe iz biotehnoloških procesa*, Hemijsko-tehnološki fakultet u Splitu, Zavod za organsku tehnologiju.

Colucci J.A., Borero E.E., Alape F. (2007). Biodiesel from an Alkaline, Transesterification Reaction of Soybean Oil Using Ultrasonic Mixing, *Journal of the American Oil Chemists' Society*, 82(7), 525-530.

Čišija V. (2013).*Uticaj ispitivanih parametara na prinos i kvalitet biodizela,* Završni rad prvog ciklusa studija, Prirodno-matematički fakultet, Sarajevo.

Gerpen J.V.(2005). Biodiesel Processing and Production. *Fuel Processing Technology,*86(10), 1097-1107.

Gogate P.R., KabadiA. M. (2009). A review of applications of cavitation in biochemical engineering/biotechnology. *Biochemical Engineering Journal*, 44(1), 60-72.

Gogate P.R. (2008). Cavitational reactors for process intensification of chemical processing applications: A critical review. *Chemical Engineering and Processing: Process Intensification,*47(4), 515-527.

Gude V.G., Patil P., Martinez-Guerra E., Shuguang D.,Nirmalakhandan N. (2013).Microwave energy potential forbiodiesel production.*Sustainable Chemical Processes,*1(1), 5.

Jurac Z. (2011).*Optimiranje proizvodnje biodizela iz otpadnih jestivih ulja s obzirom na zahtjeve kvalitete*, Doktorska disertacija, Tehnički fakultet, Sveučilište u Rijeci, Rijeka.

Kelkar M.A., Gogate P.R., Pandit A.B.(2008).Intensification of esterification of acids for synthesis of biodiesel using acousticand hydrodynamic cavitation, *Ultrasonics Sonochemistry*, 15(3), 188-194.

Lima L.P., Santos F.F., Costa E., Fernandes F.A. (2012). Production of free fatty acids from waste oil by application of ultrasound, *Biomass Conversion Biorefinery,* 2(4), 309-315.

Nielsen P.M., Brask J., Fjerbaek L. (2008). Enzymatic biodiesel production: Technical and economical considerations. *European Journalof Lipid Science Technology*, 110(8), 692–700.

Peterson C.L. (1986). Vegetable oil as a diesel fuel: Status and researchpriorities, *Transactionsof theASAE*, 29(5), 1413-1422.

Ranganathan S.V., Narasimhan S.L., Muthukumar, K.(2008). An overview of enzymatic production of biodiesel. *Bioresource Technology,*99(10), 3975-3981.

Sheehan J., Camobreco V., Duffield J., Graboski M., Shapouri, H. (1998).*Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus*; Final Report, SR-580-24089; National Renewable Energy Laboratory (NREL): Golden, CO(US).

Vatrenjak-Velagić V. (1997).*Analitička kontrola kvaliteta*, Studentska štamparija Univerziteta u Sarajevu, Sarajevo.

Young F.R. (1989).*Cavitation*, McGraw Hill, London, UK.

Wu P., Yang Y., ColucciJ.A., Grulke E.A. (2007). Effect of Ultrasonication on Droplet Size in Biodiesel Mixtures, *Journalof the American Oil Chemist Society,* 84(9), 877-884.

Zhang Y., Dube M.A., Mclean D.D., Kates M.(2003). Biodiesel production from waste cooking oil:1. Process design and technological assessment. *Bioresource Technology*, 89(1),1-16.

Summary/Sažetak

Iz dosadašnjih istraživanja vidljivo je da neprestano iscrpljivanje fosilnih goriva utiče na okoliš, a postojeće rezerve nafte dovoljne su za narednih pedesetak godina. Kako je potreba za energentima sve veća, tako se i energetska politika okreće razvoju i istraživanju obnovljivih izvora energije, među koje spada i biogorivo. Cilj ovog rada bio je istražiti postupak sinteze biodizela pomoću ultrazvuka iz biljnih ulja ispitujući uticaj odabranih parametara na proces sinteze biodizela i kvalitet istog. Sinteza biodizela rađena je iz nekorištenog suncokretovog ulja i suncokretovog ulja korištenog u fast-food-u (otpadno ulje). Posebna pažnja je posvećena djelovanju ultrazvučnog polja (kavitaciji) na proces sinteze biodizela, odnosno na hemijsku reakciju transesterifikacije. Nakon sinteza urađena su ispitivanja gustoće, viskoziteta, tačke plamišta i prinosa reakcije sinteze odgovarajućim metodama i aparaturama. Rezultati istraživanja su pokazali da je najoptimalnija temperatura reakcije transesterifikacije uz primjenu ultrazvuka na 60^0C, vrijeme djelovanja ultrazvuka od 15 minuta, te omjer alkohol-ulje 3:1. Takođe, rezultati su pokazali da upotrebom ultrazvuka u procesu sinteze biodizela, reakcija transesterifikacije može da se odvija i na znatno nižim temperaturama u odnosu na konvencionalnu sintezu biodizela, pri čemu se dobija biodizel zadovoljavajućih karakteristika.Primjenom ultrazvučnog generatora za laboratorijsku sintezu biodizela uveliko se skraćuje vrijeme trajanja sinteze, povećava se brzina reakcije, smanjuje se količina nusproizvoda - sapuna, može se koristiti manja količina alkohola i prilikom ispiranja smanjuje se problem otpadne vode i, naposlijetku, štedi se energija jer reakcija traje kraće i može da se odvija na nižim temperaturama.