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TOWARD A CIRCULAR ECONOMY: WASTE VALORIZATION FOR THE PRODUCTION OF BIODIESEL AND ENRICHED PELLETS

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Abstract: The most common model of linear economy is currently unsustainable, from the economic, energy and ecological aspects. The enormous increase in human needs for various products and energy has led to a reduction in raw material reserves, on the one hand, and the accumulation of waste, on the other. Therefore, it is necessary to widely adopt the circular economy model, where waste is treated as a raw material, with the idea of achieving zero waste production without use of virgin raw materials. In that sense, in this work food and agricultural waste was used to obtain liquid and solid biofuels. Used cooking oil was used as a raw material in the production of biodiesel, while the waste shell of a hen's egg served as the source of a catalyst for the reaction. Glycerine, as a side product of the chemical reaction, was mixed with agricultural and woody biomass in the production of enriched pellets. The fuels obtained in this way were thermodynamically characterized. For biodiesel and glycerine, the density and viscosity at atmospheric pressure and temperatures were measured, while for the mixtures of crude glycerine and biomass, the calorific value was determined. The obtained products show promising characteristics as potential energy source.
Keywords: waste eggshell, used cooking oil, crude glycerine, biodiesel, biomass, pellet

INTRODUCTION

The problems related to climate change and global warming, which are partly caused by the emission of greenhouse gases, are becoming more noticeable and serious every day. In addition to the limited reserves of fossil fuels, another issue with their use is the emission of a large amount of greenhouse gases. Therefore, intensive work is being done to replace them and to promote the use of biofuels. The combustion of biodiesel emits 11% less CO and 10% less polluting particles and the net emission of CO_2 is 78% lower than when using diesel [1,2]. Furthermore, the burning of fossil fuels to generate heat leads to the creation of huge amounts of CO_2, NO_x, SO_2 and other pollutants, which can be significantly reduced by using biomass-derived pellets.

The goal of the present research is to contribute to the practical application of the circular economy in the field of biofuel production. Biodiesel is obtained by a transesterification reaction between oil/fat and alcohol, with the presence of a catalyst, and glycerol is separated as a side product. Aiming to revalorize waste through the production of biodiesel, the basic raw material was used cooking oil, and the catalyst was obtained from the waste shell of a hen's egg [3]. Furthermore, glycerol, which is produced in significant quantities as a by-product, was further used as an additive in the production of pellets.

Commercial biodiesel production is most commonly a homogeneously catalysed transesterification reaction, where used catalyst is in liquid state. This leads to need for washing biodiesel from the liquid catalyst, where a lot of waste water is created requiring large amounts of energy and means for water purification. That can be avoided by applying a heterogeneously catalyzed reaction, i.e. using solid CaO as a catalyst. This ensures energy and economic savings and reduces the amount of generated waste, which is one of the basic postulates of the circular economy.

Eggshells are hazardous solid organic waste that is mostly accumulated without any prior treatment. The unpleasant smell of egg shell biodegradation, as well as the fact that the egg membrane attracts pests, which causes the spread of diseases, increased the need to find solutions for managing this type of waste. Eggshell contains 96–97% $CaCO_3$ with 3–4% organic matter, which indicates a huge potential for its revalorization, such as the production of CaO, which serves as a catalyst in the biodiesel production reaction [4].

Disposal of used cooking oil is a huge problem because it is most often poured into drains, which leads to clogging of sewer pipes. In addition, used cooking oil drastically reduces the efficiency of wastewater treatment plants and is extremely harmful to the aquatic ecosystem. Reusing used cooking oil in food is not recommended due to its tendency to turn into trans-fat after use, so other forms of recycling such as biodiesel production are recommended.

The present research proposes to use a catalyst obtained from waste in a very simple way, which makes it extremely cheap, and the basic raw material was also waste - used cooking oil. Thus, in addition to the economic optimization of the biodiesel production process, the problem of waste disposal is also solved, which is a significant additional benefit.

The use of crude glycerol, obtained in significant quantities during the production of biodiesel (1 kg per 10 kg of biodiesel produced), is very limited due to its impurities and variable composition. Crude glycerol is traditionally considered a low-value waste, whose disposal can have harmful impact on the environment, so the issue of its removal is extremely important. Crude glycerol can be integrated with waste biomass, such as agricultural and wood residues, to improve its properties as a fuel. Crude glycerine can serve as a binder in the production of pellets, which increases the yield and durability of pellets during storage and transportation, and also serves as a lubricant, which reduces the energy required for pelletisation. The influence of glycerol additives on the combustion of pellets has been investigated and it was concluded that the thermal efficiency of the boiler in which pellets were used remained almost the same [5,6], while the NO_x emission was significantly reduced when burning pellets with glycerol [7].

The aim of the research presented here was to contribute to environmental protection and the reduction of human impact on climate change, by applying main principles of circular economy. Waste egg shell was transferred to CaO which served as catalyst in the production of biodiesel (heterogeneous catalysis) from used sunflower cooking oil. The obtained biodiesel and crude glycerine was analysed and their thermodynamic properties were measured. The obtained glycerine was mixed with agricultural and woody biomass and the energy content of such mixtures was analyzed.

MATERIAL AND METHODS

Material

Waste hen's eggshells were provided by Melange, egg processing factory from Belgrade, R. Serbia. Used sunflower cooking oil was collected by the authors in households. Methanol was purchased from Sigma Aldrich with purity of 99.8 mol %.

Experimental

Waste hen's eggshells were collected and thoroughly cleaned and dried in an oven. The clean eggshells were crushed and converted to CaO by annealing at 1103.15 K [3]. The used cooking oil was collected, filtered through filter paper and used as the basic raw material for the production of biodiesel. Chemical composition of used oil was determined by a certified laboratory using gas chromatography with flame ionic detector. Biodiesel was synthesized from used cooking oil and methanol (molar ratio of methanol to oil was 10:1) in the presence of heterogeneous CaO catalyst. (catalyst/oil weight ratio was 5 %). Transesterification reaction was conducted in a batch reactor at 338.15 K for 2 h [3]. Biodiesel and methanol were separated from glycerol and catalyst using centrifuge and separating funnel, whereas methanol was evaporated in a rotary evaporator (Fig. 1).

Crude glycerine as a side product of the reaction was mixed with waste biomass, beech and wheat straw, in small portions, in order to examine the possibility of its use as an additive in pellet production.

Figure 1. The apparatus used for the biodiesel production

Densities and viscosities of the produced biodiesel and crude glycerine were measured by means of Stabinger viscometer (model SVM 3000/G2) at various temperatures and atmospheric pressure.

The calorific value and element analysis of the mixtures of the obtained crude glycerine and biomass was determined in Institute of nuclear sciences „Vinča“, Department of Thermal Engineering and Energy – „ITE“, Department of Thermal Engineering and Energy – „ITE“.

The samples were prepared according to method SRPS CEN/TS 14780: 2011 in a biomass mill Retsch SM 100. The calorific value and element analysis is determined according to the methods SRPS EN ISO 18125:2017 and BS EN ISO 16948: 2015 using IKA C 200 Calorimeter and LECO - CHN 628 with Sulfur module.

RESULTS AND DISCUSSION

Analysis of the composition of the used sunflower oil showed that it mostly consists of linoleic acid 54.24 g/100g, oleic acid 33.07 g/100g, palmitic acid 7.09 g/100g and stearic acid 3.58 g/100g. Gas chromatography of the obtained biodiesel proved very high yield of the reaction of 99 mas %, which confirms the good quality of the catalyst obtained from eggshell.

Density and viscosity of the obtained biodiesel were measured in temperature range (288.15 - 363.15) K at atmospheric pressure. As expected, density linearly decreases with the increase in temperature, whereas the viscosity dependence on temperature was exponential (Fig. 2). The obtained values fit within the limits prescribed by the standard for biodiesel EN 14214 [8].

The measured density and viscosity of the produced biodiesel (USME) were compared to the values obtained in the previous research for the biodiesel obtained by methanolysis of pure sunflower oil (SME) [2] and ethanolysis of pure sunflower oil (SEE) [2], and for commercial diesel fuel [9] (Fig. 2).

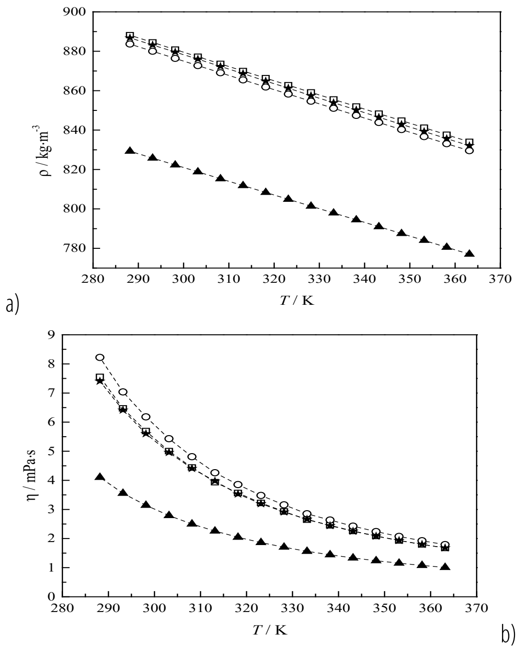

Figure 2. a) Density and b) viscosity at atmospheric pressure of (∀) SME [2], (–) SEE [2], (ξ) USME and (7) EuroDiesel [9].

It was shown that biodiesel has a higher density and viscosity compared to diesel fuel which is one of the reasons to use lower blends of biodiesel with diesel in diesel engines instead of pure biodiesel [9]. The biodiesel obtained from used sunflower oil has almost identical thermodynamic properties to that obtained from pure sunflower oil. Further, the use of ethanol (SEE) and methanol (SME) in the transesterification reaction gives biodiesels with very similar thermodynamic properties.

Density and viscosity of the produced crude glycerine were measured at temperatures (288.15 - 343.15) K at atmospheric pressure and they exhibited expected dependence on temperature (Fig. 3).

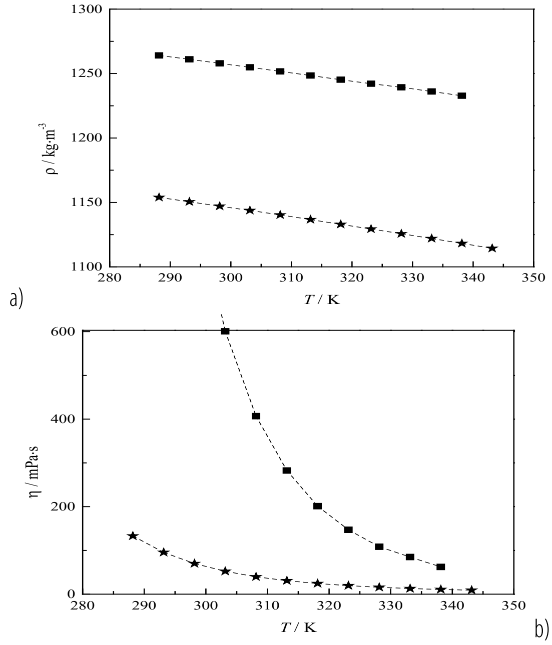

Figure 3. a) Density and b) viscosity at atmospheric pressure of (ξ) crude glycerine and (!) pure glycerine [10,11]

The measured density and viscosity of crude glycerine were compared to the values found in literature for pure glycerine [10,11]. The produced crude glycerine was significantly less dense and less viscous than pure glycerine, indicating a certain fraction of impurities in it. On the other hand, high density and viscosity are one of the main challenges when using glycerine, so in that sense crude glycerine has more desirable thermodynamic properties for wider use.

The crude glycerine was mixed with waste biomass, specifically beech and wheat straw, in the fractions of 5 mas % and 10 mas % of glycerine, aiming to investigate the possibility of producing enriched pellets from such mixtures. The studying of calorific values of the prepared mixtures showed that the addition of crude glycerine increased the calorific value. In the case of beech it was from 17.61 MJ / kg for pure wood to 17.67 MJ / kg (5 mas % of crude glycerine) and 17.85 MJ / kg (10 mas % of crude glycerine), and for wheat straw the increase was from 15.8 MJ / kg to 15.84 MJ / kg (5 mas % of crude glycerine) and 15.88 MJ /kg (10 mas % of crude glycerine).

CONCLUSION

Within the presented research, biodiesel was obtained from used sunflower oil using a catalyst obtained from a waste shell of a hen's egg. The eggshell, mainly consisting of $CaCO_3$, was converted into a CaO by annealing and the quality of the catalyst for the fatty acid transesterification reaction was confirmed by a high reaction yield of 99%. The side product of reaction, crude glycerine, was tested for use as an additive in the production of pellets.

The thermodynamic characterisation of the produced biodiesel and crude glycerine was performed in wide range of temperature at atmospheric pressure. The obtained density and viscosity of biodiesel, as well as its composition and the content of fatty acid methyl esters, met the limits prescribed by European standard for biodiesel (BS EN 14214:2012+A2:2019 [8]).

The measured density and viscosity of crude glycerine were significantly lower than those reported in literature for pure glycerine, which is favourable for its industrial use. Crude glycerine was mixed with beech and wheat straw and it increased their calorific value, indicating its great potential for use in the production of pellets.

The presented research brings mentionable economic and environmental benefits as it offers the solution for the problems, such as disposal of the waste eggshell and used cooking oil, as well as of crude glycerol by their revalorization. It also promotes the use of biofuels, both through the mixing of biodiesel with diesel fuel, and the use of enriched pellets obtained from waste biomass and crude glycerine.

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