

HIGH PRESSURE DENSITIES AND DERIVED PROPERTIES OF BIODIESEL FUEL PRODUCED BY HETEROGENEOUS TRANSESTERIFICATION FROM BIOWASTE

by

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Original scientific paper
<https://doi.org/10.2298/TSC180723178M>

High pressure density of biodiesel is a crucial parameter necessary for the Diesel engine design and performance improvement as well as proper combustion optimization. Biodiesel production utilizing biowaste as raw material reduces the capital costs and environmental problems related to biowaste disposal. In this investigation, biodiesel was synthesized in a heterogeneous transesterification reaction utilizing used cooking oil and methanol as reactants and eggshell raw material as a calcium-oxide catalyst source. Calcination was carried out at temperature 1073.15 K for 4 hours and transesterification was conducted at 338.15 K. Densities of produced biodiesel were measured at pressures up to 60 MPa and over the temperature range 288.15-413.15 K and fitted employing the modified Tammann-Tait equation. Viscosities of biodiesel are also measured at atmospheric pressure over the temperature range 288.15-338.15 K. From measured density data, important mechanical properties, such as the isothermal compressibility and the isobaric thermal expansivity, were calculated. High transesterification reaction yield was obtained (almost 99 wt.%) while densities and viscosities of analyzed biodiesel sample were in accordance with recommended standard values.

Key words: high pressure density, waste oil biodiesel, heterogeneous transesterification, isothermal compressibility, isobaric thermal expansivity, viscosity

Introduction

Fuels produced from renewable resources and/or biowaste are seen as a potential solution for oil crisis and environmental problems. Legal demands imposing the share of energy from renewable sources at least 10% in the transport sector by 2020, overlapped with environmental issues concerning biowaste disposal, have clearly defined sustainable biodiesel production as scientific and industrial priority. On the other hand, the concerns related to the biodiesel production from food crops imposed need for non-food biodiesel sources (second generation biodiesel), e.g. used cooking oils or waste animal fats. In EU the total waste cooking oil (WCO) capacity is estimated to significant amount of 700 000-1 000 000 t per year [1].

The biodiesel production plants mostly utilize traditional technology of fatty acids alkyl esters (FAAE) production. The FAAE, main constituents of biodiesel, are usually produced in transesterification reaction, which can be conducted using homogenous or heterogeneous catalyst, lipases or alternative reaction treatment such as application of ultrasound or

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supercritical conditions, *etc.* Typical transesterification reaction can be carried out at moderate temperature and atmospheric pressure with no significant capital costs and very high yield of product [2-4].

The application of homogeneous catalyst gives high yield of biodiesel although with many disadvantages. The main drawbacks are related to environmental issues and no possibility of the catalyst reuse. The biodiesel production with homogenous catalyst is usually followed with biodiesel washing, which generates large amounts of wastewater that must be treated before disposal. On the other hand, heterogeneous catalyst is easily separable, recyclable and does not create wastewater [2, 3, 5-12]. Solid base oxides, such as CaO, MgO, ZnO, BeO, lanthanum and zeolite have been used as heterogeneous catalysts. They are applied separately or in a combined mixture that is pre-treated before its application in transesterification reaction.

Among aforementioned, mostly used is CaO since it has shown a good catalytic performance in transesterification reaction [5-12]. It is low soluble in methanol so it is easily separable after reaction, cheap and environmentally friendly. Moreover, it can be produced from industrial food waste as a raw material, which disposal makes problems all over the world. The main biowaste sources of calcium-oxide are eggshells, bones or mollusk shells where it exists as calcium-carbonate.

Transesterification reaction mechanism and advantages or weaknesses of chosen reaction conditions have already been explained in [2, 5, 7, 9, 11, 13-17]. Ma and Hanna [2] described transesterification conditions and that paper was used as initial source of reaction conditions. According to Ma and Hanna [2] alkali-catalyzed transesterification is promoted by low free fatty acids (FFA) content in triglycerides and anhydrous glycerides and alcohol. In the case when water and FFA are present in triglycerides acid-catalyzed transesterification can be used. Further, Ma and Hanna [2] examined effect of temperature on yield of transesterification reaction and concluded that optimal temperature depends on the oil used but it is mostly in the range 303.15-333.15 K. Kawashima *et al.* [5] studied influence of CaO pretreatment with methanol on transesterification reaction. They found that maximum yield of FAME was obtained when CaO was activated at 298.15 K for 1.5 hours and the transesterification reaction was conducted at 333.15 K for 3 hours [5]. Taufiq-Yap *et al.* [7] investigated methanolysis of *Jatropha curcas* oil and in their case optimal temperature for transesterification was 338.15 K and the conversion of fatty acids to biodiesel were increasing gradually during the first 2 hours of reaction time and after that period remained nearly constant. Granados *et al.* [11] described production of biodiesel from sunflower oil by using activated calcium oxide and their transesterification reaction was performed for 2 hours at 333.15 K. They also considered the reutilization of the CaO for several runs and noticed that the yield of FAME was more than 90% when fresh catalytor was used and then decrease to 80% in the second run but stays at that level even after eight cycles of reutilization [11]. It is obvious that changing of specific reaction conditions may lead to smaller percentage of FAME in biodiesel sample, with same or similar quality.

There are defined standards [18, 19] to be fulfilled by produced mixture of alkyl esters of fatty acids in order to be considered biodiesel [20].

One of the most important properties for high performance of Diesel engine and proper combustion is fuel's density, especially at high pressure and temperature conditions. From the accurate density data very important derived mechanical coefficients can be calculated, *e.g.* isothermal compressibility, isobaric thermal expansion coefficient, molar isobaric heat capacity, *etc.* Biodiesel can be used in conventional or modified diesel engines, usually blended with diesel fuel.

In this work biodiesel was synthesized from WCO as a feedstock while the catalyst was prepared from eggshell waste as a raw material. Raw eggshell was characterized using thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). Transesterification was conducted at 338.15 K, with 15:1 methanol/oil molar ratio and 5 wt.% of catalyst loading. In our recent papers [21, 22] as well as in the works of other groups, high pressure density data for biodiesels produced from various vegetable oils, *e.g.* rapeseed, sunflower, soybean, palm, corn, cotton, pumpkin have been reported [3, 6, 9-11, 23]. However, no data related to WCO high pressure densities and derived properties are available. Here, densities and viscosities of biodiesel produced from WCO are reported at temperatures 288.15-338.15 K and at atmospheric pressure. Additionally, densities were measured at high pressure (up to 60 MPa) and over the temperature range from 288.15-413.15 K. From measured data the following mechanical properties were calculated: isothermal compressibility, isobaric thermal expansion coefficient, internal pressure and difference between specific heat capacity at constant pressure and at constant volume. All mentioned properties are very important for technical application of biodiesel, especially in modelling of heat and mass transfer in moving fluids [24].

Experimental section

Materials

Biodiesel investigated in this work was synthesized by transesterification reaction from WCO collected from restaurants in Serbia. Chemical composition of WCO was determined using gas chromatography with flame ionic detector (GC-FID 6890, Agilent) Column: CP-Sil 88 (100 m × 0.25 mm, film thickness 0.2 μm).

Methanol used in transesterification reaction was produced by Fischer Chemical with high purity (99.99 % mas). Eggshells that served as CaO catalyst source in biodiesel production were provided by Melange Company from Serbia.

Table 1. Chemical composition of WCO and produced biodiesel

WCO components ^a	wt.%
Palmitic	8.38
Stearic	3.42
Oleic	33.40
Linoleic	50.52
FFA content	0.82
Water content	0.06
Biodiesel composition	wt.%
FAME ^b	98.88
MG ^c	0.33
DG ^d	0.25
TG ^e	0.54
Iodine value [18]	116.2
Cetane number [25]	51
Reaction yield	99 wt.%

^a fatty acids present in traces are not shown
^b determined by applying European standard
 EN ISO 4259:2006 [25]

^c MG - monoglyceride

^d DG - diglyceride

^e TG - triglyceride

Table 1 shows weight percentage of fatty acids that are mainly present in WCO and water and FFA content, as well as the produced biodiesel composition.

Catalyst preparation and characterization

Chicken eggshells were collected from the local factory. After careful washing, it was dried in laboratory drier for 24 hours at 343.15 K, since those conditions were confirmed as optimal for preparation of sample for further use. Dry eggshells were kept in closed jars ready for grinding in a mill. Thermal behavior of raw eggshells was determined using a SDT Q600 instrument, (TA Instruments). The DSC and TGA were performed under a nitrogen flow of 100 cm³ per minute with linear temperature programming at 10 K per minute in the temperature range of 298.15-1273.15 K. Calcination of eggshells was carried out at temperature 1073.15 K [12].

Transesterification procedure

A series of tests were performed, where reaction time, calcinations temperature, molar ratio oil/methanol, catalyst amount, reaction temperature and reaction feedstock (vegetable, animal, fresh, and recycled oil) were investigated as

reaction variables, in order to find the optimal conditions for biodiesel production from WCO. Based on the gathered results and thorough review of literature the following procedure and reaction conditions, which gave the highest reaction yield, were chosen.

The transesterification reaction was conducted using the heterogeneous CaO based catalyst produced from chicken eggshells. The molar ratio of methanol to oil was 15:1, while the catalyst was added with a weight content of 5% (catalyst/oil weight ratio). Transesterification reaction was conducted in a batch reactor at 338.15 K. Catalyst and methanol were mixed in reactor until stationary conditions were achieved under methanol reflux and preheated oil was added into the reactor. Comparing reaction time and yield, it was concluded that there was no increase in yield after 2 hours of reaction, so this time was chosen as optimal reaction time. After cooling, biodiesel and methanol were separated from glycerol and catalyst using centrifuge and stratified in separating funnel. Methanol was evaporated in a rotary evaporator. Biodiesel was filtered through double filter paper.

Biodiesel characterization

The content of WCO was analysed using gas chromatography (6890, Agilent) with flame ionization detector Agilent, column CP-Sil 88 (length = 100 m, inner diameter = 0.25 mm, film thickness = 0.2 μm), in licensed laboratory, SP laboratory Novi Bečej. For evaluation of fatty acid methyl-ester content, normalization method was used (all the components of the sample are presented at chromatogram, so that total area below the peaks represents 100% of all the compounds).

The content of fatty acid methyl esters (FAME) in biodiesel was analyzed using gas chromatography with flame ionization detector model Varian 3400 by applying european standard EN ISO 4259:2006 [25], while iodine value and cetane number of obtained biodiesel were calculated according to equations presented in European standard [18, 26], respectively, tab. 1.

Based on data reported in papers [2, 16, 27] it can be assumed that cooking oil used here is a mixture of sunflower and palm oil. Amount of FFA and water is in accordance with previously suggested limits [9]. The yield was calculated in relation to product mass/WCO feedstock mass.

Density measurements at atmospheric pressure were performed using an Anton Paar DMA 5000 digital vibrating U-tube densimeter which have a stated accuracy of $\pm 5 \cdot 10^{-3} \text{ kg/m}^3$. Temperature was regulated with a built in solid-state thermostat to $\pm 0.001 \text{ K}$. Calibration of the apparatus was performed using ambient air and Millipore quality water. The combined expanded uncertainty in density was within $2 \cdot 10^{-2} \text{ kg/m}^3$. Biodiesel viscosities were measured with a digital Stabinger viscometer (model SVM 3000/G2). The temperature in the cell was regulated to $\pm 0.01 \text{ K}$ with a built in solid-state thermostat. The reproducibility of the dynamic viscosity is 0.35%, while the relative standard uncertainty in dynamic viscosity measurements was estimated to be within $\pm 1\%$ [28, 29].

Density measurements at high pressures were experimentally studied employing an Anton Paar DMA HP density measuring cell connected to an Anton Paar HP DMA 5000 vibrating tube densimeter. Details of experimental procedure are already described in our previous work [30]. The apparatus was used in temperature range 288.15-413.15 K and pressures up to 60 MPa. Each selected temperature was controlled with an integrated Peltier thermostat having stability within $\pm 0.05 \text{ K}$. Pressure in the system was measured using a pressure transducer WIKA S-10. The transducer was calibrated up to 60 MPa and the maximum value of the sums of deviation and expanded measurement uncertainty was $\pm 0.1815\%$ in relation to the full range [30]. The procedure of Comunas *et al.* [31] has been employed to calibrate the Anton Paar DMA HP densimeter.

The influence of sample's viscosity on density was estimated by using the information retrieved from a personal correspondence with the supplier Anton Paar and it was less than 0.07 kg/m^3 . The expanded uncertainty in the reported densities with confidence level of 95% ($k = 2$), estimated considering the uncertainties of pressure, temperature, oscillation period measurements and the damping effects on the vibrating tube, is 0.8 kg/m^3 in the temperature range 288.15-363.15 K and 2.0 kg/m^3 at temperatures 373.15-413.15 K.

Density correlation and calculation of derived properties

Experimental values of densities were fitted to the modified Tammann-Tait equation. This correlation involves fitting parameters a_i , b_i , and c_i and relates density, ρ , with temperature, T , and pressure, p , according to the eqs. (1)-(4):

$$\rho(T,p) = \frac{\rho^{\text{ref}}(T)}{1 - C(T) \ln \left[\frac{B(T) + p}{B(T) + p^{\text{ref}}} \right]} \quad (1)$$

$$\rho^{\text{ref}}(T) = \sum_{i=0}^2 a_i T^i \quad (2)$$

$$B(T) = \sum_{i=0}^2 b_i T^i \quad (3)$$

$$C(T) = \sum_{i=0}^2 c_i T^i \quad (4)$$

where ρ^{ref} is density at reference pressure, p^{ref} . In our case the parameter C is treated as temperature independent.

From density data valuable derived properties can be calculated.

Isothermal compressibility, κ_T , describes the effect of a pressure on density at constant temperature as follows [32, 33]

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (5)$$

Isobaric thermal expansion coefficient, α_p , expresses the temperature influence on a fluid density at constant pressure and can be calculated by using the following equation [31, 32]:

$$\alpha_p = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \left(\frac{\partial p}{\partial \rho} \right)_T^{-1} = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (6)$$

Also, using experimental density at high temperatures and pressures, the difference between specific heat capacity at constant pressure, c_p , and specific heat capacity at constant volume, c_v , could be calculated [32, 33]:

$$c_p = c_v + T \frac{\left(\frac{\partial p}{\partial T} \right)_p^2}{\rho^2 \left(\frac{\partial p}{\partial \rho} \right)_T} = \frac{\alpha_p^2 T}{\rho \kappa_T} \quad (7)$$

Additionally, the thermal pressure coefficient, γ , presenting the ratio between isobaric thermal expansibility and isothermal compressibility is determined [32, 33]:

$$\gamma = \frac{\alpha_p}{\kappa_T} \quad (8)$$

From the isobaric thermal expansion coefficient and the isothermal compressibility coefficient the internal pressure, p_{int} , can be determined as follows [32, 33]:

$$p_{\text{int}} = \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_p - p = T\gamma - p = \frac{T\alpha_p}{\kappa_T} - p \quad (9)$$

Internal pressure describes the intermolecular interactions and represents the change of internal energy during isothermal expansion or contraction.

Results and discussion

TGA/DSC

Figure 1 shows weight loss –1 and endothermic peak –2 for eggshell that occurs at temperatures around 1073.15 K, which corresponds to the results reported previously [10, 15]. This loss is attributed to decomposition of CaCO_3 and out gassing of CO_2 . Organic compounds and water are lost at temperatures below 673.15 K.

Catalyst calcined at 1073.15 K gave very high yield of FAME, almost 99 wt.%. Viriya-Empikul *et al.* [10] also reported that optimum calcination temperature is 1073.15 K, while higher calcination temperatures cause severe sintering of catalyst particles, resulting in suppressed smaller active sites and consequently smaller biodiesel yields. Wang *et al.* [34] suggest that the basest sites are in the interior of catalyst, since surface of the catalyst shows low porosity. Khemthong *et al.* [8] reported that derived eggshell is dense material due to its very low surface area and pore volume with very high basic site density which makes it active for transesterification reaction. Besides, it is important to point out that activation of catalysts just before the reaction plays important role in biodiesel yield, since remove of gaseous water molecules creates high porosity [15].

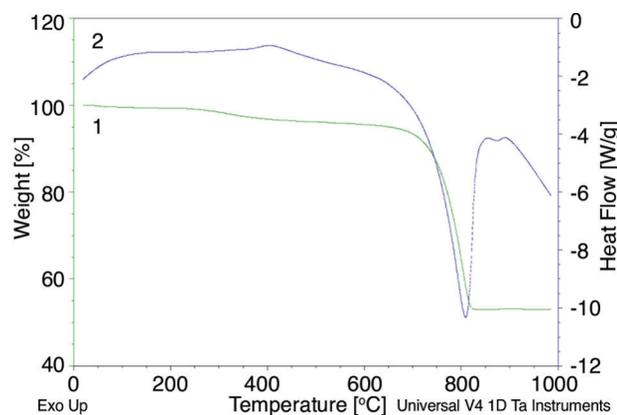


Figure 1. TGA (1) and DSC (2) curves of raw eggshell

Densities and viscosities of biodiesel at atmospheric pressure

Table 2 shows densities and viscosities of biodiesel sample over the temperature range 288.15 to 338.15 K and at atmospheric pressure. It is obvious that both, density and viscosity, decrease with temperature increase. Biodiesel sample meets the density demand from standards EN 14214 [18] and ASTM D6751 [19], which recommends the density range of 860-900 kg/m^3 at 288.15 K. According to EN 14214 [18] standard biodiesel kinematic viscosity at 313.15 K should be in range 3.5-5.0 mm^2/s , while by ASTM D6751 [19] acceptable range is 1.9-6.0 mm^2/s . Produced biodiesel has the kinematic viscosity near upper limit of EN 14214 [18] standard, 4.9567 mm^2/s , but fulfil the ASTM D6751 standard [19]. According to this and to the values presented in tab. 1, the produced mixture of WCO methyl esters meets the most of relevant

conditions, *i.e.* referent values for the properties studied in this work, to be called biodiesel.

The knowledge of biodiesel viscosity at atmospheric pressure allows prediction of viscosity values at high pressures using the method proposed by Freitas *et al.* [35]:

$$\ln \eta = \ln \eta_0 + a \frac{p - p_0}{T^b} \quad (10)$$

where η_0 [mPa·s] stand for the dynamic viscosity at reference pressure p_0 (0.1 Mpa), T [K] and p [MPa] denote absolute temperature and absolute pressure, respectively. Fitting parameters a and b have the values $1.2 \text{ K}^{0.84} \text{ Pa}^{-1}$ and 0.84, respectively [35].

Densities and derived properties at pressures up to 60 Mpa

Densities of the biodiesel were measured at pressures 0.1-60 Mpa and at temperatures 288.15-413.15 K and are given in tab. 3.

Experimental density data were fitted to the modified Tammann-Tait equation. For the optimization of a_i , b_i , and c_i parameters reference pressure was set to 1 MPa, while Marquardt's algorithm was applied in order to minimize the objective function, *i.e.* standard deviation σ :

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2}{N - m}} \quad (11)$$

where ρ^{exp} and ρ^{cal} stand for experimentally determined density and density calculated by eq. (1), respectively, N is the number of experimental data and m represents the number of parameters included in the modified Tammann-Tait equation. The adjusted fitting parameters are given in tab. 4 along with the corresponding standard deviation.

Figures 2(a) and 2(b) depict dependencies of the isothermal compressibility, κ_T , and the isobaric thermal expansion coefficient, α_p , on pressure along isotherms for examined biodiesel, respectively. As it was expected, both κ_T and α_p decrease with the increase in pressure at isothermal conditions whereas at lower temperatures the pressure influence is less pronounced.

Curves of isothermal compressibility at higher temperatures have more parabolic shapes compared to almost linear form at lower temperatures. The κ_T values lay between 0.47 and 1.36 GPa^{-1} . The former values correspond to pressure 60 MPa and temperatures 293.15 K, while the latter correspond to 0.1 MPa and 413.15 K.

Values of the isobaric thermal expansion coefficient are ranging $(0.66-0.92) \cdot 10^{-3} \text{ K}^{-1}$ at investigated temperature and pressure ranges. Lower α_p values are favored since larger isobaric expansion coefficient means a larger engine power loss because of fuel heating [36]. Additionally, α_p isotherms show an intersection point around 45 MPa, at this point α_p is temperature independent. At pressures lower than at the intersection point, α_p increases with temperatures rise, while the temperature influence is opposite at higher pressures. For the biodiesel analyzed in the work of Schedemann *et al.* [37] the same behavior occurs having the intersection point at pressure

Table 2. Densities and viscosities of produced biodiesel sample within the temperature range from 288.15-338.15 K and at atmospheric pressure [18]

T [K]	ρ [kgm^{-3}] ^a	η [mPa·s] ^b
288.15	883.76	8.492
293.15	880.08	7.222
298.15	876.42	6.311
303.15	872.77	5.522
308.15	869.13	4.866
313.15	865.49	4.290
318.15	861.87	3.868
323.15	858.24	3.482
328.15	854.63	3.150
333.15	851.02	2.838
338.15	847.42	2.629

^a EN 14214 [18] and ASTM D6751 [19] limits for density at 288.15 K: 860-900 kg/m^3

^b EN 14214 [18] limits for kinematic viscosity at 313.15 K: 3.5-5.0 mm^2/s
 ASTM D6751 [19] limits for kinematic viscosity at 313.15 K: 1.9-6.0 mm^2/s

around 65 MPa, while in the work of Dzida and Prusakiewicz [38] the intersection point is in accordance with ours, approximately at 40 ± 5 Mpa.

Table 3. Experimental values of density for produced biodiesel sample at pressures up to 60 MPa within the temperature range from 293.15-413.15 K

ρ [kg·m ⁻³]							
T [K]							
p [MPa]	293.15	298.15	303.15	308.15	313.15	318.15	323.15
0.1	880.2	876.6	872.9	869.2	865.6	862.0	858.3
1	880.7	877.1	873.5	869.8	866.2	862.6	858.9
5	883.0	879.5	875.9	872.3	868.8	865.2	861.6
10	885.9	882.4	878.9	875.3	871.9	868.3	864.8
15	888.6	885.2	881.7	878.2	874.9	871.4	868.0
20	891.3	887.9	884.5	881.1	877.8	874.4	871.1
25	893.9	890.6	887.3	883.9	880.6	877.3	874.0
30	896.5	893.2	889.9	886.6	883.4	880.1	876.9
35	899.0	895.7	892.5	889.2	886.1	882.8	879.7
40	901.4	898.2	895.0	891.8	888.7	885.4	882.4
45	903.7	900.6	897.4	894.3	891.2	888.0	885.0
50	906.0	902.9	899.8	896.7	893.6	890.5	887.5
55	908.2	905.1	902.0	899.0	895.9	892.8	889.9
60	910.3	907.3	904.2	901.2	898.2	895.1	892.2
p [MPa]	333.15	343.15	353.15	363.15	373.15	393.15	413.15
0.1	851.1	843.8	836.5	829.2	821.6		
1	851.7	844.5	837.2	830.0	822.7	808.1	793.4
5	854.5	847.4	840.3	833.2	826.1	811.8	797.5
10	857.9	850.9	844.0	837.1	830.1	816.3	802.4
15	861.2	854.4	847.6	840.8	834.1	820.6	807.1
20	864.4	857.7	851.1	844.4	837.9	824.7	811.6
25	867.4	860.9	854.4	847.9	841.5	828.7	815.9
30	870.4	864.0	857.7	851.3	845.0	832.5	820.1
35	873.3	867.0	860.8	854.6	848.4	836.2	824.0
40	876.1	869.9	863.8	857.7	851.7	839.7	827.8
45	878.8	872.7	866.7	860.7	854.8	843.0	831.3
50	881.4	875.4	869.5	863.6	857.7	846.1	834.7
55	883.9	878.0	872.1	866.3	860.6	849.2	837.9
60	886.3	880.5	874.7	868.9	863.2	852.0	840.9

Temperature and pressure influence on the internal pressure, was also examined. It is evident from eq. (9) that internal pressure represents the change of internal energy during isothermal expansion or contraction. As temperature increases internal pressure decreases. However, the influence of pressure is rather different. Up to 343.15 K internal pressure decreases with pressure rise, while at higher temperatures 393.15 and 413.15 K as pressure increases values of internal pressure also increase fig. 3. Prieto *et al.* [38] performed thorough analysis of temperature and pressure influence on internal pressure for 19 fuels of different compositions. It

was presented that for temperatures between 283.15 K and 373.15 K and pressures up to 40 MPa values of internal pressure were in the range 281 MPa and 386 MPa with the average minimum and maximum values at 304 and 367 MPa for 19 analyzed fuels. In fig. 3 the influence of temperature on the internal pressure for the produced biodiesel at 0.1 MPa is presented, since at this pressure changes are most pronounced. The internal pressure at atmospheric pressure deviates from about 360-311 MPa in temperature range 293.15-373.15 K, which is in good agreement with the results presented in the work of Prieto *et al.* [39]. Analyzing the values of internal pressures and cohesion pressure Prieto *et al.* [39] concluded that biodiesel behaves as non-associated liquid with no strong molecular interactions.

Table 4. Fitting parameters of Tait equation for produced biodiesel sample and the corresponding standard deviation σ

a_0 [kgm ⁻³]	1089.49
a_1 [kgm ⁻³ K ⁻¹]	-0.70187
a_2 [kgm ⁻³ K ⁻²]	-3.54726·10 ⁻⁵
b_0 [MPa]	466.1915
b_1 [MPaK ⁻¹]	-1.55320
b_2 [MPaK ⁻²]	1.41048·10 ⁻³
c_0	8.89240·10 ⁻²
σ [kg m ⁻³]	0.087

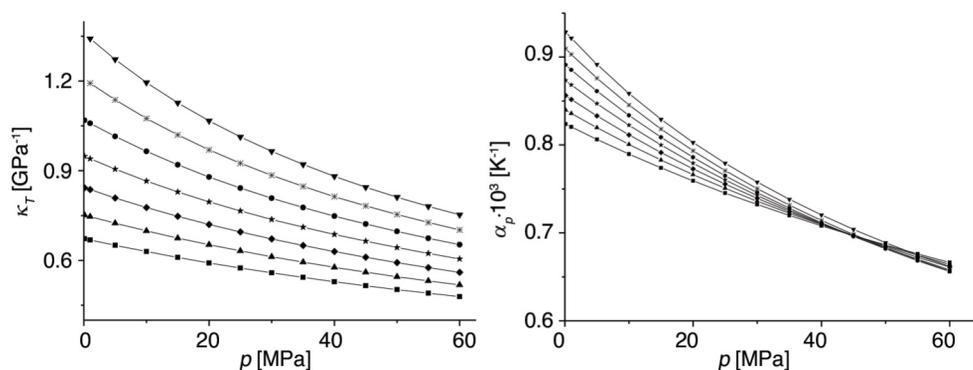


Figure 2. (a) Isothermal compressibility and (b) isobaric thermal expansion coefficient of produced biodiesel sample vs. pressure at; (■) 293.15 K, (▲) 313.15 K, (◆) 333.15 K, (★) 353.15 K, (●) 373.15 K, (✱) 393.15 K and (▼) 413.15 K, Lines are guides for eyes

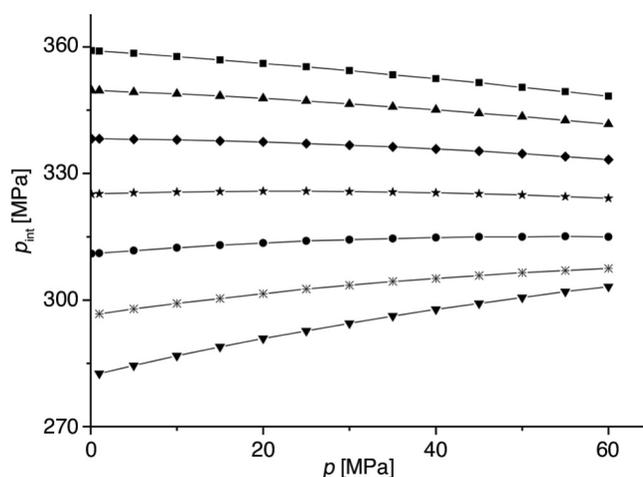


Figure 3. Internal pressure of produced biodiesel sample vs. pressure at; (■) 293.15 K, (▲) 313.15 K, (◆) 333.15 K, (★) 353.15 K, (●) 373.15 K, (✱) 393.15 K and (▼) 413.15 K, Lines are guides for eyes

Conclusions

Biodiesel was synthesized in heterogeneous transesterification reaction from waste cooking oil and methanol. CaO based catalyst was produced by calcination of the eggshells at 1073.15 K and analyzed using TGA/DSC. Viscosities and densities of the produced biodiesel sample were determined at atmospheric pressure over the temperature range 288.15-338.15 K. Additionally, densities of biodiesel were measured at pressures up to 60 MPa over the temperature range 288.15-413.15 K and fitted using the modified Tammann-Tait equation. From measured density data the isothermal compressibility, the isobaric thermal expansion coefficient, the internal pressure and the difference between specific heat capacity at constant pressure and at constant volume are calculated. Calculated isobaric thermal expansion coefficient ranges $(0.66-0.92) \cdot 10^{-3} \text{ K}^{-1}$ showing an intersection point around 45 MPa. Internal pressure deviates from about 360-282 MPa at temperatures 293.15-413.15 K and at atmospheric pressure.

High reaction yield (almost 99 wt.%), as well as high percentage of FAME in the biodiesel product and its thermodynamic and mechanical properties confirm that biodiesel can be efficiently produced from biowaste in heterogeneous transesterification reaction.

Supplementary material*

Supplementary data associated with this article can be found, in the online version.

- Figure S1 - densities and viscosities of biodiesel sample over the temperature range 288.15 to 338.15 K and at atmospheric pressure
- Figure S2 - experimental densities of analyzed biodiesel sample at pressures from atmospheric up to 60 MPa over the temperature range 288.15 to 413.15 K
- Figure S3 - the influence of temperature on the internal pressure for the produced biodiesel at 0.1 MPa
- Table S1 - High pressure viscosities calculated using eq. (10) for produced biodiesel
- Table S2 - derived thermodynamic properties: the isothermal compressibility (κ_T), the isobaric thermal expansion coefficient (α_p), the difference between specific heat capacities ($c_p - c_v$) and the internal pressure (pint).

Acknowledgment

The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Education, Science and Technological Development (project No 172063 and IP-1-38), Serbia and the Faculty of Technology and Metallurgy, University of Belgrade. Additionally, the authors are grateful for help received from ArumDec and Melange companies from Serbia in providing raw material, waste cooking oil and eggshells necessary for the experimental work.

References

- [1] Carrero, A., Perez, A., Advances in Biodiesel Quality Control, Characterization and Standards Development, in: *Advances in Biodiesel Production: Processes and Technologies*, (Eds. Luque, R., Melero, J.A), Woodhead Publishing Series in Energy, Cambridge, UK, 2012, pp. 91-130
- [2] Ma, F., Hanna, M., Biodiesel Production: a Review, *Bioresour. Technol.*, 70 (1999), 1, pp. 1-15
- [3] Leung, D. Y. C., *et al.*, A Review on Biodiesel Production Using Catalyzed Transesterification, *Appl. Energy*, 87 (2010), 4, pp. 1083-1095
- [4] Santacesaria, E., *et al.*, Main Technologies in Biodiesel Production: State of the Art and Future Challenges, *Catal. Today*, 195 (2012), 1, pp. 2-13
- [5] Kawashima, A., *et al.*, Acceleration of Catalytic Activity of Calcium Oxide for Biodiesel Production, *Bioresour. Technol.*, 100 (2009), 2, pp. 696-700

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- [6] Ngamcharussrivichai, C., *et al.*, Ca and Zn Mixed Oxide as a Heterogeneous Base Catalyst for Transesterification of Palm Kernel Oil, *Appl. Catal. A-Gen.*, *341* (2008), 1-2, pp. 77-85
- [7] Taufiq-Yap, Y. H., *et al.*, Calcium-Based Mixed Oxide Catalysts for Methanolysis of Jatropha Curcas Oil to Biodiesel, *Biomass Bioenerg.*, *35* (2011), 2, pp. 827-834
- [8] Khemthong, P., *et al.*, Industrial Eggshell Wastes as the Heterogeneous Catalysts for Microwave-Assisted Biodiesel Production, *Catal. Today*, *190* (2012), 1, pp. 112-116
- [9] Kouzu, M., *et al.*, Heterogeneous Catalysis of Calcium Oxide Used for Transesterification of Soybean Oil with Refluxing Methanol, *Appl. Catal. A-Gen.*, *355* (2009), 1-2, pp. 94-99
- [10] Viriya-Empikul, N., *et al.*, Biodiesel Production Over Ca-Based Solid Catalysts Derived from Industrial Wastes, *Fuel*, *92* (2012), 1, pp. 239-244
- [11] Granados, M. L., *et al.*, Biodiesel from Sunflower Oil by Using Activated Calcium Oxide, *Appl. Catal. B-Environ.*, *73* (2007), 3-4, pp. 317-326
- [12] Wei, Z., *et al.*, Application of Waste Eggshell as Low-Cost Solid Catalyst for Biodiesel Production, *Bioresour. Technol.*, *100* (2009), 11, pp. 2883-2885
- [13] Miladinovic, M., *et al.*, Heterogeneous Base-Catalyzed Methanolysis of Vegetable Oils: State of Art, *Hem. Ind.*, *64* (2010), 2, pp. 63-80
- [14] Glišić, S., *et al.*, Biodiesel Synthesis at High Pressure and Temperature: Analysis of Energy Consumption on Industrial Scale, *Bioresour. Technol.*, *100* (2009), 24, pp. 6347-6354
- [15] Hu, S., *et al.*, Utilization of Waste Freshwater Mussel Shell as an Economic Catalyst for Biodiesel Production, *Biomass Bioenerg.*, *35* (2011), 8, pp. 3627-3635
- [16] Yan, S., *et al.*, Oil Transesterification Over Calcium Oxides Modified with Lanthanum, *Appl. Catal. A-Gen.*, *360* (2009), 2, pp. 16-170
- [17] Granados, M. L., *et al.*, Leaching and Homogeneous Contribution in Liquid Phase Reaction Catalysed by Solids: The Case of Triglycerides Methanolysis using CaO, *Appl. Catal. B-Environ.*, *89* (2009), 1-2, pp. 265-272
- [18] ***, BS EN 14214:2012 + A1:2014. Liquid Petroleum Products - Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications - Requirements and Test Methods.
- [19] Barabas, I., Todorut, I. A., Biodiesel Quality, Standards and properties. in: *Biodiesel-Quality, Emissions and by-Products*, (Eds. Montero, G., Stoytcheva, M.,) In tech, Rijeka, Croatia, 2011, pp. 3-28
- [20] Lois, E., Letter to the Editor, *Fuel*, *86* (2007), 7-8, pp. 1212-1213
- [21] Ivaniš, G. R., *et al.*, Biodiesel Density and Derived Thermodynamic Properties at High Pressures and Moderate Temperatures, *Fuel*, *165* (2016), Feb., pp. 244-251
- [22] Ivaniš, G. R., *et al.*, Thermodynamic Properties of Biodiesel and Petro-Diesel Blends at High Pressures and Temperatures. Experimental and Modeling, *Fuel*, *184* (2016), Nov., pp. 277-288
- [23] Hua Tan, Y., *et al.*, The Potential of Waste Cooking Oil - Based Biodiesel Using Heterogeneous Catalyst Derived from Various Calcined Eggshells Coupled with an Emulsification Technique: A Review on the Emission Reduction and Engine Performance, *Renew. Sust. Energ. Rev.*, *47* (2015), July, pp. 589-603
- [24] Lampreia, I. M. S., Nieto De Castro, C., A New and Reliable Calibration Method for Vibrating Tube Densimeters Over Wide Ranges of Temperature and Pressure, *J. Chem. Thermodyn.*, *43* (2011), 4, pp. 537-545
- [25] ***, ISO 4259:2006. Petroleum Products - Determination and Application of Precision Data in Relation to Methods of Test
- [26] Lukic, I., *et al.*, Kinetics of Sunflower and Used Vegetable Oil Methanolysis Catalyzed by CaO·ZnO, *Fuel*, *113* (2013), Nov., pp. 367-378
- [27] Knothe, G., Fuel Properties of Highly Polyunsaturated Fatty Acid Methyl Esters. Prediction of Fuel Properties of Algal Biodiesel, *Energ. Fuel.*, *26* (2012), 8, pp. 5265-5273
- [28] Živković, E. M., *et al.*, Volumetric and Viscometric Behavior of the Binary Systems Ethyl Lactate + 1,2-Propanediol, + 1,3 - Propanediol, + Tetrahydrofuran and + Tetraethylene Glycol Dimethyl Ether. New UNIFAC-VISCO and ASOG-VISCO Parameters Determination, *Fluid Phase Equilib.*, *373* (2014), July, pp. 1-19
- [29] Knežević-Stevanović, A. B., *et al.*, Thermodynamic and Spectroscopic Study of the Ternary System Dimethyladipate + Tetrahydrofuran + 1-Butanol at $T = (288.15 \text{ to } 323.15) \text{ K}$, *J. Chem. Eng. Data*, *58* (2013), 11, pp. 2932-2951
- [30] Ivaniš, G. R., *et al.*, An Apparatus Proposed for Density Measurements in Compressed Liquid Regions at Pressures of 0.1-60 MPa and Temperatures of 288.15-413.15 K, *J. Serb. Chem. Soc.*, *80* (2015), 8, pp. 1073-1085
- [31] Comunas, M. J. P., *et al.*, Density of Diethyl Adipate Using a New Vibrating Tube Densimeter from (293.15 to 403.15) K and up to 140 MPa. Calibration and Measurements, *J. Chem. Eng. Data*, *53* (2008), 4, pp. 986-994

- [32] Safarov, J., *et al.*, Thermodynamic Properties of Standard Seawater: Extensions to High Temperatures and Pressures, *Ocean Sci*, 5 (2009), July, pp. 235-246
- [33] Ivaniš, G. R., *et al.*, Modeling of Density and Calculations of Derived Volumetric properties for N-Hexane, Toluene and Dichloromethane at Pressures 0.1-60 MPa and Temperatures 288.15-413.15 K, *J. Serb. Chem. Soc.*, 80 (2015), 11, pp. 1423-1433
- [34] Wang, X., *et al.*, Experimental and Analytical Study on Biodiesel and Diesel Spray Characteristics Under Ultra-High Injection Pressure, *Int. J. Heat Fluid Flow*, 31 (2010), 4, pp. 659-666
- [35] Freitas, S. V. D., *et al.*, Measurement and Prediction of High-Pressure Viscosities of Biodiesel Fuels, *Fuel*, 122 (2014), Apr., pp. 223-228
- [36] Pratas, M. J., *et al.*, Biodiesel Density: Experimental Measurements and Prediction Models, *Energ. Fuel*, 25 (2011), 5, pp. 2333-2340
- [37] Schedemann, A., *et al.*, Measurement and Correlation of Biodiesel Densities at Pressures up to 130 MPa, *Fuel*, 107 (2013), May, pp. 483-492
- [38] Dzida, M., Prusakiewicz, P., The Effect of Temperature and Pressure on the Physicochemical Properties of Petroleum Diesel Oil and Biodiesel Fuel, *Fuel*, 87 (2008), 10-11, pp. 1941-1948
- [39] Prieto, N. M. C. T., *et al.*, Correlation and Prediction of Biodiesel Density for Extended Ranges of Temperature and Pressure, *Fuel*, 141 (2015), Feb., pp. 23-38