

The Effect of Operating Parameters of Alkali Catalyzed Transesterification of Sunflower Oil With Methanol in the Presence of the Cosolvent Assisted by Hydrodynamic Cavitation on the Degree of Triglyceride Conversion

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The effect of operating parameters of alkali catalyzed transesterification of sunflower oil with methanol in the presence of the cosolvent assisted by hydrodynamic cavitation on the degree of triglyceride conversion

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Abstract

Method of independent variation of the value of one operating parameter has been used to investigate the effect of operating parameters on alkali-catalyzed transesterification of sunflower oil with methanol in presence of tetrahydrofuran (THF) as cosolvent, assisted by hydrodynamic cavitation (ACTC) on the value of the degree of triglyceride conversion (DTC). ACTC was performed by a venturi-type hydrodynamic cavitation reactor (VCR) of our construction. To determine the effect of ACTC on DTC following operating parameters were varied: reaction mixture inlet pressure (p_1) from 202.3 kPa to 1013.2 kPa; methanol to oil molar ratio (M_1) from $M_1=3$ to $M_1=12$; concentration of catalyst (C_c) from 0.3wt% to 1.5wt%; methanol to THF molar ratio (M_2) from $M_2=1.25$ to $M_2=2.0$; temperature (T) from 20°C to 55°C, number of passes through the VCR (n) from $n=1$ to $n=10$. It was found, based on the obtained results, that: a) the values of DTC increase with the increase in p_1 , M_1 , C_c , and n , b) the values of the DTC decrease with the increase in T and c) maximum values of the DTC are obtained at $C_c=1.0\sim 1.1\text{wt}\%$ and $M_2=1.5$.

Keywords: hydrodynamic cavitation, operating parameters; transesterification; venturi type reactor; cavitation yield

Running title: Double-intensified transesterification of sunflower oil with methanol

1. Introduction

Biodiesel is an environmentally friendly alternative fuel, as it is renewable, biodegradable, non-toxic, and has substantially reduced sulfur oxides and carbon monoxide emissions. Most typically it is produced by alkaline or acid-catalyzed transesterification reaction of various vegetable oils with short-chain alcohols, mainly methyl alcohol [1]. The reaction rate in transesterification reactions is limited by mass transfer because reaction takes place in a liquid-liquid two-phase system since oils and methyl alcohol are immiscible. Therefore, achieving a higher reaction rate by increasing the efficiency of the oil, methanol, and catalyst contact is crucial to perform the reaction in the reactor of economic size. Regarding this problem, several technologies of process intensification can be applied for increasing contact of two liquid phases and mass transfer rate, consequently [2].

Alkaline catalysis and acid catalysis are conventional methods for biodiesel production. Since transesterification is an equilibrium reaction, alcohol is used in excess to shift the reaction towards the formation of fatty acid methyl esters (FAME) [1]. Alkaline catalyzed process, the most commonly worldwide used industrial process, is strongly affected by mixing and stirring, both of which increase the contact area between the reactants. Having limitations of classical procedures in mind, there has been a strong urge to evolve a novel, time and cost-saving, efficient, and environmentally friendly biodiesel process of production, superior to now existing classical procedures [3].

Considering whether the catalyst remains or not in the same, liquid, phase as the reactants, the catalysts can be either homogenous or heterogeneous. Alkaline homogenous catalyzed process: a) operates on low temperatures and pressures; b) gives higher levels of triglyceride conversion in shorter periods, 60 minutes mostly reported; c) has higher catalytic activity at low catalyst concentrations; d) is easily available and cheap. The downsides of the process are: a) requires high purity oil; b) sensitivity to higher free fatty acid and water content; c) catalyst cannot be reused and d) costly separation of the reaction products. Acidic homogenous catalyzed process: a) uses low-cost oils; b) alcohol is used as a solvent and esterification reagent, leading to separation and transesterification in one step; c) has a lower sensibility to free fatty acid content in the oils. On the other hand, process: a) is more sensitive to the content of water in the oil; b) there is significant equipment corrosion; c) produces more waste and unintended byproducts; d) requires higher temperatures; e) requires longer reaction times; f) has weaker catalytic activity. Heterogeneous catalysis has several upsides: a) catalyst

separation and reuse are easy; b) lower cost of catalyst; c) process has a lower impact on the environment; d) no soap formation. The downside of heterogeneous catalysis is that process requires high temperatures, up to 200°C, making the process considerably expensive [4].

One way to intensify transesterification reaction is enhancing the miscibility of oil and methanol, thus turning the reaction system from two-phase to one-phase, which can be done by adding a cosolvent. This way, the reaction system doesn't need additional stirring, and separation of glycerin phase, after the completion of transesterification, is several times faster. Various cosolvents have been reported: different light ethers, acetone, hexane, heptane, CO₂, and several ionic liquids. The most frequently used cosolvent is tetrahydrofuran (THF), due to its low price, non-toxicity, and non-reactivity [2, 5, 6, 7]. Boocock et al. [8] performed alkali catalyzed transesterification of soybean oil by methanol and with THF as cosolvent, at ambient temperature, at $M_1=6$ and $M_2=1,25$. They found that with THF as cosolvent, the system shifted to one phase, thus shortening reaction time significantly. Banković-Ilić et al. [9] found out that although the addition of THF as cosolvent has positive influences on hydrodynamic properties of the reaction mixture, the addition of cosolvent in excess leads to change in reaction kinetics from models with mass transfer limitations towards irreversible and/or reversible second-order kinetics. Mao et al. [5], investigating transesterification of soybean oil by methanol, with cosolvent THF, at ambient temperatures, $M_1=6$, with NaOH, KOH, and MeO-Na⁺ as catalysts, found out that the reaction rate is very fast at the beginning, while the system is one-phase, but slows down rapidly after formation of the two-phase system due to glycerin formation. Ataya et al. [6] examined canola oil transesterification using acid or base catalyst in a two-phase system and one-phase system with THF as cosolvent. The authors stated that a one-phase reaction has first-order chemical reaction kinetics and that in a one-phase reaction medium there is no mass transfer resistance. Roosta and Sabzpooshan [10] used mathematical modeling to predict the use of cosolvent and confirmed that adding cosolvent does not affect the final yield of FAME, only speeds up the reaction. Encinar et al. [7] examined the effect of various cosolvents on rapeseed oil alkali catalyzed transesterification, also varying M_1 and methanol to cosolvent ratios, catalyst concentrations, temperature, and agitation speed, observing high FAME yields in short reaction times for all the different system setups. The authors also concluded that the kinetics of the reaction can be described with the pseudo-first-order kinetic model.

Intensification in alkali catalyzed transesterification of oil can be also obtained by alternating energy sources for the reaction process. High gravity [11, 12], ultrasound [13, 14,

15], hydrodynamic cavitation [3, 13, 16~25], and microwaves [26~31] were investigated, both in a laboratory and commercial scale. Beljić Durković et al. [26] examined comparative kinetics of the alkali catalyzed sunflower oil methanolysis with THF as cosolvent under conventional and microwave heating. Authors concluded that microwave heating does not affect the kinetic model of alkaline catalyzed sunflower oil methanolysis with THF as cosolvent, the isothermal value of the rate of the transesterification under microwave heating is 2.5-3.5 larger than the rate of the transesterification under conventional heating, and that microwave heating causes a significant increase in the value of the preexponential factor.

Alkali catalyzed transesterification of oil with methanol by venturi-type hydrodynamic cavitation reactor was investigated by several researchers. Maddikeri et al. [22] examined biodiesel synthesis by interesterification of waste cooking oil intensified by the plate with orifices and two different types of venturi cavitation reactors by varying reaction mixture inlet pressure, the molar ratio of oil to methyl acetate, and concentration of catalyst. Ladino et al. [32] did a numerical study of geometrical properties of venturi cavitation reactors used for biodiesel production to find the best possible venturi configuration. Chitsaz et al. [24] used response surface methodology to optimize biodiesel production from sunflower waste frying oil by VCR. Bargole et al. [33] studied the intensification of biodiesel synthesis from waste cooking oil by use of circular venturi and several different plates with orifices. Simpson et al. [34] developed several computational fluid dynamic models to simulate various venturi-type cavitation flows to provide data to be used for designing and optimizing venturi-type hydrodynamic cavitation reactors. In their review on advances and perspectives in controlled hydrodynamic cavitation Panda et al. [35] compared venturi and plate of orifices cavitation reactors and suggested that VCRs produce more stable cavitation, more cavities in number and size thus leading to better cavitation yields.

As far as the best knowledge of the authors, there is no literature data about the effect of the operating parameters of the hydrodynamic cavitation assisted alkaline catalyzed transesterification of refined sunflower oil with methanol, in presence of cosolvent, on the degree of triglyceride conversion. Considering that, the main goal of here presented work was the determination of the effects of operating parameters: reaction mixture inlet pressure, methanol to oil molar ratio, the concentration of catalyst, temperature, methanol to THF molar ratio, and the number of passes through the VCR on the degree of triglyceride conversion, in ACTC conditions, performed by here presented VCR of own construction and make.

2. Materials and methods

2.1. Materials

For the present work, the following materials were used: refined sunflower oil (AD Dijamant, Zrenjanin, Serbia), methanol (CH_3OH , $\geq 99\%$, p.a., Merck, Darmstadt, Germany), tetrahydrofuran (THF, 99 %, p.a., J.T. Baker, Deventer, Holland), potassium hydroxide (KOH, $\geq 85\%$, p.a., Analytica LTD, Czech Republic), acetic acid (CH_3COOH , analytical purity, Zorka AD, Šabac, Serbia). The fundamental physicochemical properties of sunflower oil used in given experiments are shown in Table 1[26]:

Table 1. The physicochemical properties of refined sunflower oil

Physicochemical property	Value
Palmitic acid	6.6 wt%
Stearic	5.1 wt%
Oleic	19.6 wt%
Linoleic	68.7 wt%
Free fatty acid	0.02 wt%
Saponification value	193.7 (mg KOH/g)
Iodine value	130.4 (mg I ₂ /g)
Water	0.05 (mg/g)

2.2. Hydrodynamic cavitation-assisted alkaline catalyzed transesterification (ACTC)

Alkaline catalyzed transesterification of sunflower oil in presence of cosolvent was performed by the VCR of our construction. The schematic diagram of hydrodynamic cavitation equipment and the VCR geometric construction are respectively shown in Figure 1 (a) and (b).

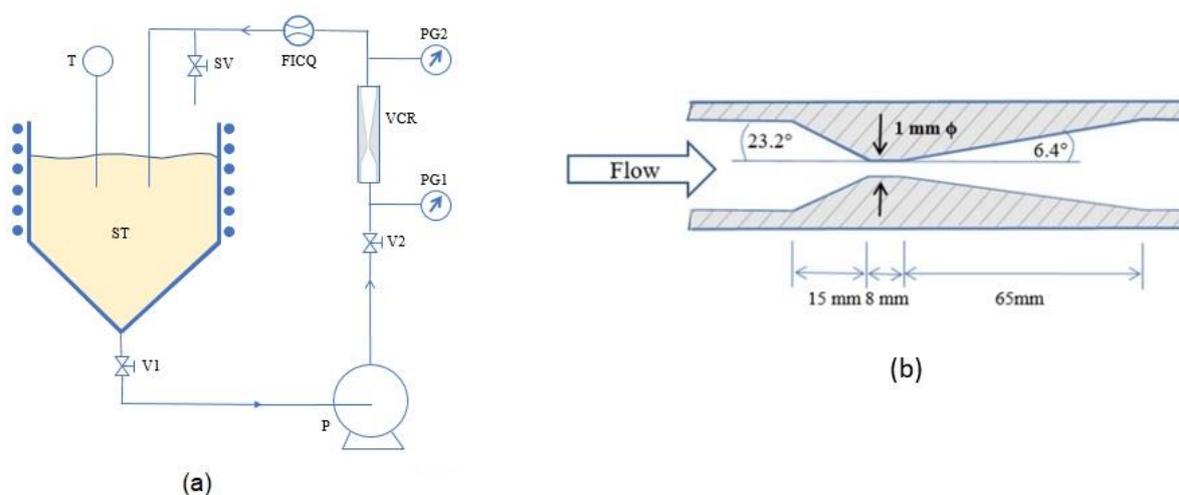


Figure 1. (a) The schematic diagram of hydrodynamic cavitation equipment (storage tank (ST), manual valves (V1 and V2), voltage regulated pump (P) (power 120 W), pressure gauges (PG1 and PG2), venturi type hydrodynamic cavitation reactor (VCR), flow meter (FICQ), sampling valve (SV), thermometer (T)); (b) The VCR geometric construction

Geometric characteristics of VCR are given in Table 2:

Table 2. VCR geometric characteristics

Venturi length	8 mm
Diameter throat	1mm
Length of the convergent section	15mm
Length of the divergent section	65mm
Half angle of the convergent section	23.2°
Half angle of the divergent section	6.4°

The experimental procedure of transesterification was performed as follows: refined sunflower oil (300 mL) was dosed into the storage tank and the predetermined mass of cosolvent THF was added to achieve the required methanol to THF molar ratio (1.25 – 2.0). A mixture of oil and THF was heated to previously designated T (25°C - 50°C). The previously calculated mass of catalyst KOH was dissolved in a predetermined mass of methanol to achieve a certain value of methanol to oil ratio (3 - 12) and concentration of catalyst (0.3 – 1.5wt%). The resulting solution was heated to a predetermined temperature, as same as for oil and THF

mixture, and dosed into the storage tank. The one-phase reaction mixture thus formed was loaded into the VCR by an electrical pump at the predetermined reaction mixture inlet pressure (202.3 kPa - 1013.2 kPa) for a determined time, to achieve a previously determined number of passes through the VCR (1 to 10). Since hydrodynamic cavitation increases the temperature of the reaction mixture, the temperature was maintained by the external cooling of the storage tank and regularly measured by the thermometer.

During the ACTC, predefined samples were taken from the reaction mixture, to be analyzed, at the sampling valve (SV). To stop the reaction the 1wt% acetic acid (corresponding to the amount of KOH used) was added until the neutral pH was reached. The mixture was transferred into a separating funnel and left for two hours to allow the gravitational separation of glycerin. Upon removal of glycerin from the funnel, FAME was washed for 15 minutes with warm redistilled water heated to 40 °C (volume ratio 1:1 to FAME), at 600 rpm. Then, the liquid was poured into a second separation funnel and left for several minutes to separate the water from FAME. Upon the separation and removal of the water layer, traces of residual water and residual methanol were removed by heating FAME at 105 °C.

The effects of reaction mixture inlet pressure (202.3 kPa-1013.2 kPa), methanol to oil molar ratio (3-12), the concentration of catalyst (0.6wt%-1.5wt%), reaction temperature (20°C-55°C), methanol to THF molar ratio (1.25-2.0) and the number of passes through the VCR (1-10) were investigated by the method of independent variation of the value of one operating parameter with all the other values of parameters maintained constant. All the experiments were conducted thrice and the average values were reported.

2.3. Determination of concentration of methyl esters in transesterification product

The determination of methyl esters concentration was performed by a method of gas chromatography following EN 14103:2003 [51]. The method of determining concentrations is thoroughly described in the work of Beljić Durković et al. [26].

The methyl ester concentration (C_{me}) given in percentage (wt%) was calculated using the Eq. 1:

$$C_{me} = \left(\frac{(\sum A) - (A_{ei} - A_{er})}{A_{ei} - A_{er}} \right) \cdot \left(\frac{C_{ei} \cdot V_{ei}}{m} \right) \cdot 100 \quad (1)$$

ΣA being the total peak area from the methyl ester C14 to that in C24:1, A_{ei} the peak area corresponding to the methyl heptadecanoate, A_{er} the peak corresponding to the methyl heptadecanoate of the referent sample, C_{ei} the concentration of the methyl heptadecanoate solution being used, V_{ei} the volume of the solution of methyl heptadecanoate used, and m the weight of the sample.

2.4. Determination of the converted triglycerides weight

Determination of the weight of the converted triglycerides (W_{tg}), was calculated by the Eq.2:

$$W_{tg} = \frac{M_{tg} \cdot w_i \cdot C_{me}}{3 \cdot M_{me}} \quad (2)$$

M_{tg} is the molar mass of triglycerides, w_i is the initial weight of triglycerides in the reaction mixture, C_{me} is the concentration of methyl esters, and M_{me} is the molar mass of methyl esters.

2.5. Determination of the degree of triglyceride conversion

The DTC was calculated by the following Eq. 3:

$$\text{DTC (\%)} = \frac{W_{tg}}{w_i} \cdot 100 \quad (3)$$

3. Results and discussion

3.1. The effect of inlet pressure of reaction mixture on the degree of triglyceride conversion

The inlet pressure of the reaction mixture in a venturi-type hydrodynamic cavitation reactor has the most dominant effect on the cavitation efficiency and the degree of DTC. To determine the effect of the inlet pressure of reaction mixture on the DTC, the ACTC was performed by varying the values of p_1 , in the range from $p_1=202.6$ kPa to $p_1=1013.2$ kPa, keeping values of all the other parameters constant: $M_1=6$; $M_2=1.6$; $C_c=1$ wt%; $T=20$ °C; $n=10$. Figure 2. shows the effect of inlet pressure on the degree of triglyceride conversion.

and physicochemical processes are most commonly studied in the literature [36]. Mechanical effects of cavitation include processes of turbulence generation within the reaction system, mass transfer improvement, homogenization of reaction mixture, improvement in the solid phase dispersion, microjet occurrence, and shock wave impact. Thermal effects are associated with the existence of high-temperature local areas (hot spots) and chemical effects with activation of reactant molecules, ionization of molecules, in-molecule chemical bond break-ups, and forming of free radicals in the reaction system. Although there is no available data in the literature, to the best of our knowledge, concerning the effect of inlet pressure on the values of DTC in ACTC processes assisted by cosolvents, it should be beneficial to take the closest related results into account for the comparison.

A similar effect of the reaction mixture inlet pressure on the yield of biodiesel was showed by Maddikeri et al. [22] in the study of alkali catalyzed interesterification of waste cooking oil with methyl-acetate using the VCR, where it was shown that an increase in inlet pressure from 200 kPa to 300 kPa, increases the biodiesel yield up to 89%. Also, Ghayal et al. [16] in a study of the alkali catalyzed transesterification of waste frying oil assisted by hydrodynamic cavitation showed that the reaction mixture inlet pressure of 300 kPa was required to achieve the 94% degree of the conversion of triglycerides to methyl esters.

It was established that an increase in the value of DTC with reaction mixture inlet pressure is caused by the increase in turbulent flow velocity of the reaction mixture through the venturi-type hydrodynamic cavitation reactor. This leads to the decrease in hydrodynamic cavitation reactor's cavitation number and increases in the reactor's cavitation effectivity due to an increase in the number of the bubbles that collapsed; the amplitudes of pressure and temperature impulses; the energy of collapsing bubble; the generated shock wave intensity. As a consequence, the values of DTC increase. The experimentally obtained results in this work, that transesterification does not occur at $p_1 \leq 304.0$ kPa under given conditions, implies that ACTC reaction does not happen inside the core of the cavity or at the interphase region between the cavity and bulk reaction mixture, which explains why there are no small intermediary molecules or radicals in the reaction products. Most likely, an extremely high rate of ACTC reaction is a consequence of a significant increase in reactant mass transfer which, in response, significantly accelerates the reaction.

3.2. The effect of methanol to oil molar ratio on the degree of triglyceride conversion

Eckey and Am [37], Sridharan and Mathai [38], proposed a mechanism of conventional alkaline catalyzed transesterification of oil with various types of alcohols. Following that mechanism, the transesterification of oil with alcohol is a complex reaction that consists of three elemental consecutive reverse reactions. Due to this, to achieve higher conversion and FAME yield, conventional transesterification is performed with methanol to oil molar ratio M_1 much higher than the stoichiometric molar ratio of methanol and oil $M_1=3$.

The effect of M_1 on the value of DTC has been investigated by performing experiments at different values of M_1 , within a range from $M_1=3$ to $M_1=12$, while all the other values of parameters were maintained constant: $p_1=1013.3$ kPa; $M_2=1.6$; $C_c=1$ wt%; $T=20^\circ\text{C}$; $n=10$. The effect of methanol to oil molar ratio on the degree of triglyceride conversion is shown in Figure 3.

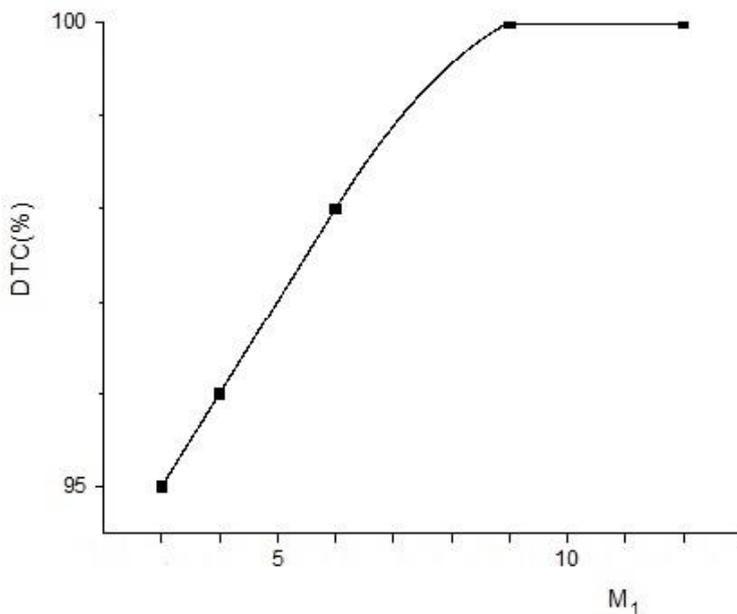


Figure 3. The dependence of the degree of triglyceride conversion from methanol to oil molar ratio

As it can be seen from the results shown in Figure 3, the value of DTC linearly increases with the increase in value M_1 from $M_1=3$ to $M_1=9$. The dependence can be mathematically described by Eq. 4:

$$DTC=92.67 + 0.83M_1, R^2=0.99 \quad (4)$$

At values of $M_1 \geq 9$, under conditions of alkaline catalyzed transesterification with methanol assisted by hydrodynamic cavitation, complete conversion of oil into methyl esters was accomplished. Just like in the case of the obtained results for the effect of reaction mixture inlet pressure on the value of DTC, there are no available literature data, to the best of knowledge of the authors, about this issue of the effect of M_1 on the values of the DTC in ATCT processes assisted by the cosolvents. Mohod et al. [25] presented the results of the effect of M_1 on the degree of triglyceride conversion of alkali catalyzed transesterification of fresh and waste cooking sunflower oil assisted by hydrodynamic cavitation via high-speed homogenizer, and established that a value of DTC=54 % has been achieved at $M_1=3$; $T=45$ °C; $t=120$ min. The values of DTC increased in a complex manner with an increase in M_1 . The here found effect of M_1 on the value of DTC, under ACTC, confirms our previous assumption that in ACTC conditions transesterification reaction does not occur in the cavity core or at the interphase region between the cavity and bulk liquid but within the mass of the liquid, without diffusion limitations, and with a significant increase in the value of the boundary surface of the interaction. The reaction is therefore very fast (between 5s and 1min) at $T=20$ °C and stoichiometric methanol to oil ratio.

3.3. The effect of catalyst concentration on the degree of triglyceride conversion

Catalyst concentration in the reaction mixture, as well as p_1 and M_1 , has a significant impact on transesterification rate, the DTC, and FAME yield. To investigate the effect of catalyst concentration on the DTC, the ACTC was conducted at different C_c values, ranging from $C_c=0.6$ wt% to $C_c=1.5$ wt%, with keeping constant all the other parameters: $p_1=1013.2$ kPa; $M_1=3$; $M_2=1.6$; $T=20$ °C; $n=10$. Figure 4. shows the effect of the concentration of catalyst on the degree of triglyceride conversion.

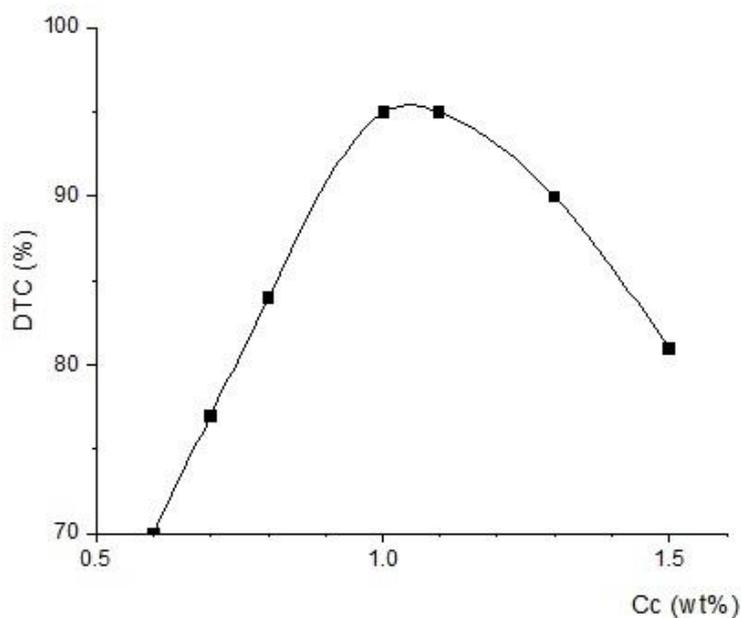


Figure 4. The dependence of the value of the degree of triglyceride conversion from the concentration of catalyst

As the results presented in Fig 4. imply, the dependence of the DTC vs. C_c has a complex shape. For the values of C_c within the range $0.6\text{wt}\% \leq C_c \leq 1.0\text{wt}\%$ the DTC value increases with the increase in the value of C_c from DTC=70% to DTC=95%. On the contrary, for the values of $C_c \geq 1.1\text{wt}\%$, the DTC values decrease with the increase in C_c values. The existence of the maximum for the DTC value obtained at $1.0 \leq C_c \leq 1.1\text{wt}\%$ is an indication of the optimal concentration of catalyst on ACTC. Similar results for the dependency of the DTC vs. C_c were notified by several authors, Shu et al. [39], Chuah et al. [17], Mohod et al. [25], Kolhe et al. [21] for the investigated alkaline catalyzed conventional transesterifications of various types of oils with methanol, under the conditions of cavitation, which were performed by using various types of the hydrodynamic cavitation reactors.

In conditions of a one-phase reaction system, there is neither methanol solubility in oil limitations nor is alkoxide reaction with the carbonyl group of triglycerides limited by the size of the interface area, but both are limited by the number of available alkoxide molecules which react with triglyceride molecules, forming tetrahedral intermediates such as alkyl esters and other glycerides. Therefore, following previously said, the increase in the value of DTC, due to the increase in the concentration of the catalyst within the range $0.6\text{wt}\% \leq C_c \leq 1.0\text{wt}\%$, is caused by the increase in the number of active molecules of alkoxide in the reaction mixture.

The maximum value of DTC achieved within a narrow range of catalyst concentration $1.0\text{wt}\% \leq C_c \leq 1.1\text{wt}\%$ indicates the optimum concentration of active molecules in the reaction mixture. The decrease in the values of DTC with further increase in the concentration of catalyst, from $C_c=1.1\text{wt}\%$ to $C_c=1.5\text{wt}\%$ can be explained as a consequence of the increase of the rate of saponification reaction and subsequent soap formation, which has a negative effect on the degree of triglyceride conversion.

3.4. The effect of temperature on the degree of triglyceride conversion

To understand the effect of temperature on the value of DTC, the ACTC of sunflower oil was performed at different temperatures, in the range from $T=20\text{ }^\circ\text{C}$ to $T=55\text{ }^\circ\text{C}$, with other values of parameters being constant: $p_1=1013.2\text{ kPa}$; $M_1=3$; $C_c=1\text{wt}\%$; $M_2=1.6$ and $n=10$.

Figure 5. shows the effect of temperature on the degree of triglyceride conversion.

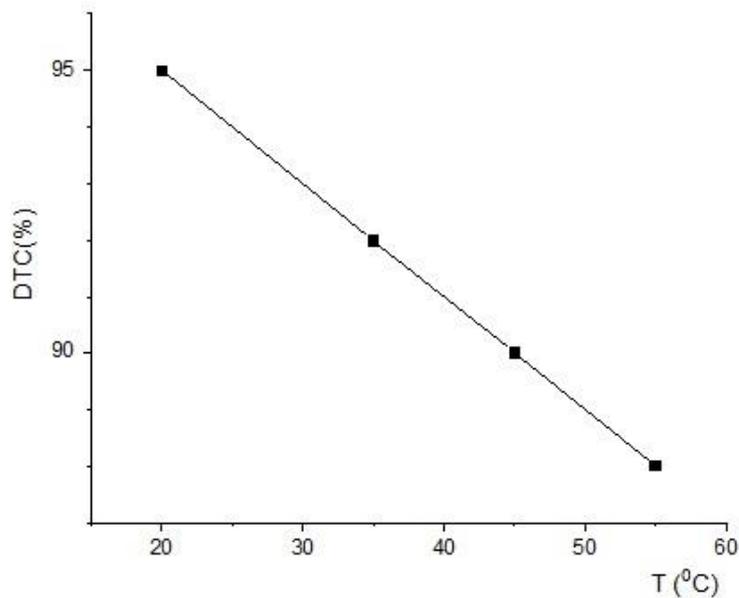


Figure 5. The dependence of the degree of triglyceride conversion from temperature

The obtained results reveal that with the increase of temperature within the investigated range, the value of DTC shows a clear linear decrease from $\text{DTC}=95\%$ at $T=20\text{ }^\circ\text{C}$ to $\text{DTC}=88\%$ at $T=55\text{ }^\circ\text{C}$. The dependence can be mathematically described by Exp. 1:

$$DTC=99 - 0.2T, R^2=1 \quad (1)$$

The influence of temperature on the rate and yield of a chemical reaction that takes place under conditions of hydrodynamic cavitation is complex and it is defined by the simultaneous influence of temperature on the rate of a chemical reaction and on physicochemical properties of the reaction mixture: vapor pressure (p_v); coefficient of viscosity (η) and coefficient of surface tension (γ), which affect the dynamics of forming, growth and implosion of the cavitation bubbles. In the case where the increase of temperature does not induce significant changes in the values of physicochemical properties of the reaction mixture, the rate and yield of the reaction under conditions of hydrodynamic cavitation should increase with the increase in temperature. In contrast to that case, when a temperature change induces significant changes in the values of physicochemical properties of the reaction mixture, the effect of temperature on the rate and yield is difficult to predict. In that case, the effect of temperature on the rate and yield of the reaction is associated with a change in a) the number of cavitation bubbles; b) dynamics of formation, growth, and the implosion of cavitation bubbles and c) collapse energy of cavitation bubbles caused by the changes in values of p_v , η and γ . It is known that the increase of temperature leads to an exponential growth of vapor pressure, thus increasing the probability of the cavitation phenomenon. Consequently, as the temperature increases: a) the number of collapsing bubbles; b) quantity of vapor inside the bubble and c) critical cavity radius, rise as well, all of which decrease collapse energy of bubbles and impair cavitation efficiency. A decrease of the value of the coefficient of viscosity due to the increase in temperature leads to the increase of the critical size of stable bubbles and the decrease in the number of cavitation events and collapse energy of bubbles, thus leading to an abrupt decrease in the cavitation efficiency. The decrease of the value of the surface tension coefficient of the reaction mixture which happened due to the temperature increase causes a) drop in the pressure value needed for bubble generation; b) increase in initial bubble radius and c) decrease of collapse energy of bubbles, and all of them result in the decrease in the cavitation efficiency.

The linear decrease of the value of DTC due to the increase in temperature, at ACTC, indicate that the most dominant effect on the value of DTC has the effects associated with the changes in physicochemical properties of the reaction system which cause the changes in cavitation bubble dynamics leading to the decrease in cavitation efficiency i.e. DTC. The result obtained by this investigation is not in agreement with the previously established effect of the temperature increase on the DTC in alkali catalyzed transesterification assisted by hydrodynamic cavitation, reported in the works presented by Rashid et al. [40] via using capillary millichannel reactor, Chuah et al. [17] via using hydrodynamic cavitation plate with

orifices reactor and Mohod et al. [25] by utilization of high-speed homogenizer, where has been concluded that DTC values increase with the increase in temperature. They explained their results by the enhancement of methanol in oil solubility and the improvement of the contact of methanol and oil due to the increase in the temperature.

3.5. The effect of methanol to THF molar ratio on the degree of triglyceride conversion

The methanol to THF molar ratio has a remarkable effect on the kinetics of conventional alkaline catalyzed transesterification of oils with alcohols because the presence of co-solvent in the reaction system determines the conditions of complete dissolution of methanol and catalysts in oil (one phase system) in which there is a significant increase of transesterification rate [8]. To investigate the effect of the molar ratio of methanol to THF on the value of DTC, ACTC was performed with different values of M_2 , ranging from $M_2=1.25$ to $M_2=2.0$, with other values of parameters being constant: $p_1=1013.2$ kPa; $M_1=3$; $T=20$ °C; $C_c=1$ wt%; $n=10$. Figure 6. shows the effect of methanol to THF molar ratio on the degree of triglyceride conversion.

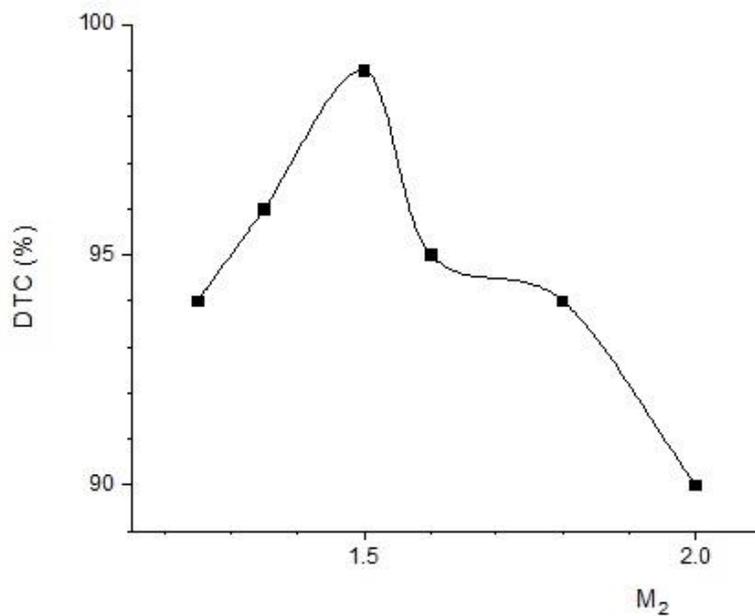


Figure 6. The dependence of the degree of triglyceride conversion from methanol to THF molar ratio

The dependence of the DTC vs. M_2 has a complex shape. The maximum value of the DTC=99% is obtained at $M_2=1.5$. This value corresponds to the value most often cited in the

literature, where complete mixing of oil, alcohol, and THF occurs and so does the formation of a one-phase system. Any deviation from this value, either in terms of increase or decrease in value outside the range results in a decrease in the value of DTC. Reduction in the value of M_2 results in a higher concentration of THF in the reaction mixture, thus leading to a rise in a) the number of bubbles; b) quantity of THF vapors within the bubble; c) bubble critical radius, all of them, consequently, bring about a decrease in collapse energy of bubbles and decrease in cavitation efficiency. In contrast, at $M_2 > 1.5$, the increase in the M_2 value relative to those required to form a single-phase system, changes back the reaction condition into a two-phase system, which also results in a decrease in the cavitation efficiency and DTC.

3.6. The effect of the number of passes through cavitation reactor on the degree of triglyceride conversion

The duration of a transesterification reaction under conventional conditions represents one of the dominant parameters affecting the value of DTC. In ACTC extended duration of transesterification is in relationship with the increase in the number of reaction mixture's passes through the VCR. To establish the effect of the number of passes on the degree of triglyceride conversion, ACTC transesterification was performed with different values of n , in a range from $n=1$ to $n=10$, while all the other values of parameters were maintained constant: $p_1=1013.2$ kPa; $M_1=3.0$; $T=25^\circ\text{C}$; $M_2=1.6$; $C_c=1\text{wt}\%$. Figure 7. shows the effect of the number of passes through the venturi-type hydrodynamic cavitation reactor on the degree of triglyceride conversion.

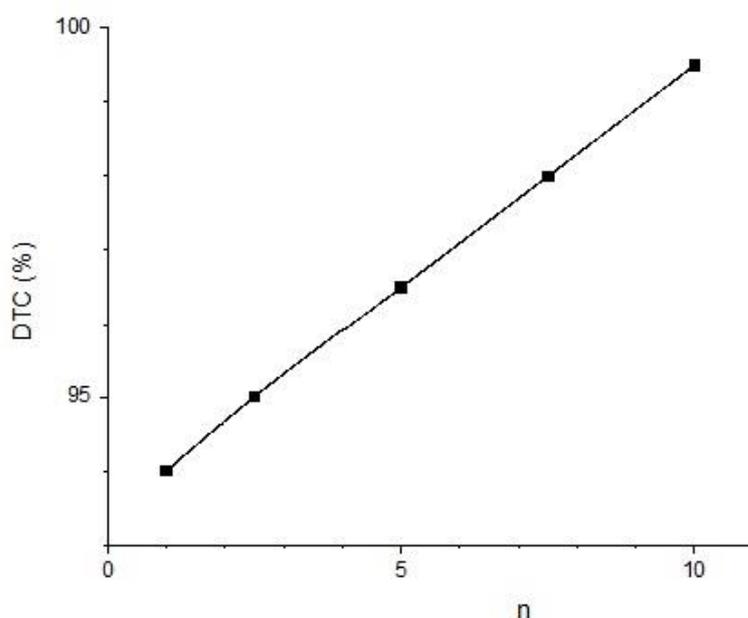


Figure 7. The dependency of the degree of triglyceride conversion from the number of passes through the venturi type hydrodynamic cavitation reactor

The degree of triglyceride conversion increases linearly with an increase in the value of n , from DTC=94%, at $n=1$ (5s) to DTC=99%, at $n=10$ (1min). The dependence can be mathematically described by Exp 2:

$$DTC=93.44 + 0.61n, R^2=1. \quad (2)$$

The increase of DTC with an increase of n is the consequence of the increase in the number of collapsing bubbles with the increase in the number of reaction mixture's passes through the cavitation device.

3.7. Cavitation yield

The application of hydrodynamic cavitation leads to a significant intensification of the chemical reaction due to: reaction time reduction, reaction yield increase, use of less forcing conditions (T, p), changes in reaction pathways resulting in increased selectivity [22]. To quantify the extent of intensification of the examined reaction/process due to the application of hydrodynamic cavitation relative to other procedure performances, a new quantity is introduced: cavitation yield (CY) [16]. Cavitation yield is defined as the yield of the product

per unit of energy supplied to the system. Table 3. presents the change of cavitation yield with changes in the values of the DTC and the number of passes through the VCR.

Table 3. The effect of DTC and n on the cavitation yield

n	t (s)	DTC (%)	CY (g/J)
1	6	94	0.528
2.5	15	95	0.213
5.0	30	97	0.109
7.5	45	98	0.073
10	60	99	0.056

The value of cavitation yield decreases with the increase in the DTC values and n from CY=0.528 g/J, at DTC=94% and $n=1$, to CY=0.056 g/J, at DTC=99% and $n=10$. Obtained values of the cavitation yield of ACTC are considerably larger than values of CY previously reported in publications for alkaline catalyzed transesterification of frying oil [16] and waste cooking oil [22] with methanol assisted by hydrodynamic cavitation ($1.28\text{-}1.22 \cdot 10^{-3}$ g/J) which indicates that ACTC represents an energy-efficient process for biodiesel production.

4. Conclusions

The effect of operating parameters of alkali catalyzed transesterification of sunflower oil with methanol, in presence of cosolvent THF, assisted by hydrodynamic cavitation, on the value of the degree of triglyceride conversion by the method of independent variation of the value of one parameter was found, for the first time in literature to the best knowledge of the authors, by here presented work. At $p_1 < 304.0$ kPa, as well as $C_c < 0.3\text{wt}\%$, there is no ACTC reaction. The increase in M_1 from $M_1=3$ to $M_1=9$ and the increase of n from $n=1$ to $n=10$ both lead to a linear increase in the value of DTC. The increase of T causes a linear decrease in the value of DTC. The increase in p_1 results in the complex increase of the value of DTC. Maximum values of the DTC are obtained at $M_2=1.5$ and $C_c=1.0\text{-}1.1\text{wt}\%$, respectively.

The variation of the operational parameters of ACTC results in the changes of a) the number of cavitation bubbles in the reaction mixture; b) dynamics of generation and growth and the implosion of cavitation bubbles and d) cavitation bubble's energy of collapse, which

explains the effect on the values of DTC. By calculating CY values ACTC was proved to be currently the fastest, simplest, energetically and economically most efficient technology for biodiesel production.

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ABBREVIATIONS

ACTC – alkaline catalyzed transesterification of refined sunflower oil with methanol in presence of tetrahydrofuran as cosolvent, assisted by hydrodynamic cavitation

DTC – the degree of triglyceride conversion FAME – fatty acid methyl esters

CY – cavitation yield VCR – venturi type hydrodynamic cavitation reactor

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