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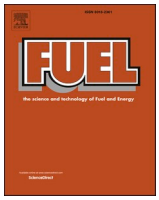

Full Length Article

Kinetic parameters of transesterification of rapeseed oil with butanol using dolomite as heterogeneous catalyst

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ABSTRACT

We analyzed the kinetic parameters of rapeseed oil transesterification with butanol using dolomite as a heterogeneous catalyst under the optimal conditions that we previously determined. At 5.24 wt% dolomite, 110 °C, and a 13.71:1 M ratio of butanol to oil, we found that the reaction followed an irreversible pseudo-first-order model, which we successfully implemented in an Aspen Plus simulation software to design the model of kinetic reactor. In addition, we proposed purification steps for the reactive mixture within the same model to produce biodiesel following requirements of standard EN 14214.

1. Introduction

Biodiesel, obtained from vegetable oil or fatty waste, is increasingly used to replace mineral fuels in various countries of the world [1]. This is related to the depleting quantities of mineral raw materials and the increasing importance of reducing environmental pollution, which is reflected in the already accepted and considered United Nations and EU documents, which call for reducing the amount of GHG emissions into the atmosphere and increasing the use of renewable resources in energy and transport. The aim is to reduce GHG emissions by 55 % by 2030 compared to 1990 [2]. The influence of the transport sector on the contribution on climate change is one of the biggest [3]. Therefore, it is consistently called for to increase the amount of biofuels in the transport sector. Diesel engines use methyl or ethyl esters of fatty acids, the synthesis of which is not complicated and is implemented industrially. It is also important that biodiesel can be used in a mixture with mineral diesel without any additional modifications to the engine and fuel system [4].

Synthesis of biodiesel is a catalytic process during which high molecular weight lipid chains are broken down due to the replacement of trihydroxyl alcohol – glycerol – with low molecular weight alcohol from one lipid molecule with the formation of three molecules of methyl or ethyl esters of fatty acids and the separation of glycerol [5]. Recently, greater attention of researchers to heterogeneous catalysts, which would be suitable for biodiesel synthesis. The advantages of their use compared to homogeneous catalysts would be that it would be easier to separate the catalysts from the reaction product and at the same time purify the product, the possibility of regenerating the catalysts and using them several times [6,7]. This reduces environmental pollution with sewage, reduces the amount of waste, energy and material costs decrease. CaO and MgO are known to be among the most commonly used heterogeneous catalysts in biodiesel production. Dolomite, a naturally occurring mineral composed mainly of calcium and magnesium carbonates, is inexpensive, non-toxic, and environmentally friendly. Since it contains both Ca^{2+} and Mg^{2+} ions, dolomite can be a precursor for biodiesel synthesis. When exposed to high temperatures, dolomite thermally decomposes into MgO and CaO. As determined by our previous research, dolomite is characterized by good catalytic efficiency in the transesterification reaction. Under optimal conditions, using this catalyst, it is possible to obtain more than 96.5 % of esters [8,9].

The synthetic methanol most often used in biodiesel synthesis is obtained from natural gas. It could be replaced by butanol, which is obtained from natural resources by the action of microorganisms. Butanol is less corrosive and less soluble in water than methanol — resulting in better miscibility with the oil phase—its application in biodiesel production has not been widely investigated [10,11]. The use of butanol in the transesterification of oils offers several advantages compared to methanol or ethanol. Its longer carbon chain enhances both the fuel properties of the resulting biodiesel and its compatibility with conventional diesel. For example, fatty acid butyl esters possess a higher

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energy content than their methyl or ethyl ester counterparts due to the presence of additional carbon atoms [12]. The conducted studies showed that the transesterification of oil with butanol can be carried out both using homogeneous catalysts and heterogeneous catalysts including enzymes. Using dolomite and biobutanol, biodiesel can be obtained from exclusively natural resources [8,13].

Unfortunately, there are little studies regarding transesterification of oils using butanol let alone kinetic data. This stops the ability to design, optimize and assess the possibility to utilize such processes in the industry. Kinetic modeling helps to predict reaction mechanisms and reaction rates which are necessary to scale up laboratory processes for designing and sizing reactors, ensuring that they can handle the desired throughput while maintaining optimal reaction conditions. But reactors are not the only equipment in technologies, so further process modeling leads to integration of kinetic data alongside other processes (filtration, separation, purification and others) and more holistic understanding of the entire process. In this case Aspen Plus is a vital tool and robust platform for simulating and optimizing complex processes efficiently and effectively. While Aspen Plus is a powerful and widely respected tool for process simulation, mastering all its features requires a significant investment in time and training. The most abundant models for biodiesel production are made particularly for methanolysis process and both Aspen Plus as well as HYSYS were used for this task. Since homogeneous transesterification with alkaline catalysts is the most common, most models use rigorous approach for designing the reactor and avoid using the kinetic data. Sotoft et al. [14] investigated enzymatic biodiesel production plant using methanol in yield model reactor while Okullo and Tibasiima [15] modeled biodiesel production from Jatropha Curcas seed oil utilizing conversion reactor. While those models deal with flowsheets and their overall economic evaluation, kinetic data is not present. Second order irreversible models are applied in studies of Souza et al [16], Boon-anuwat et al [17] and Costa et al [18]. Modeling of heterogeneous kinetics is much less common and usually pseudo first order kinetics is preferred when trying to regress experimental data [19–22]. The most challenging task in creating process flowsheet is obtaining and specifying physical properties of participating compounds. This limits not only modeling itself, but possibility of utilizing various reaction mechanisms and steps, because various scientists use pure triolein as substitute for various oils and present transesterification reaction as one step without saponification. Methanol and its organic derivatives in methanolysis processes are analyzed and specified quite well in Aspen software and some papers try to present as accurate models as possible with addition of experimentally determined physical properties of all materials. Adeniyi et al 2018 [23] introduces ANOVA as an additional tool trying to optimize the yield of biodiesel and implements it together with Aspen Plus. Silva and de Andrade [24] managed to specify the composition of various oils as accurately as possible and uses various methods to determine thermophysical properties of compounds which enables to model transesterification process with separate steps of reactions. As we can establish, models can always be improved as there is more and more kinetic and thermodynamic data about analyzed processes. But information about butanol esters is scarce now so modeling in Aspen software is very challenging nevertheless very needed because of the assessment of its applicability and sustainability.

This study aims to investigate the use of dolomite and butanol in the transesterification of rapeseed oil assessing optimal conditions and achieving highest yield of biodiesel. Performed mathematical modelling can be used for next level physical modelling, which could bring investigated process closer to larger scale industrial applications, especially considering mass and heat transfer phenomena. Since high temperature streams are used, energy consumption considerations would be welcome to assess investigated process not only from chemical but also from economic standpoint. Additionally, there is very little information about modelling heterogeneous transesterification, so this model is of significant interest.

2. Materials and methods

2.1. Transesterification of rapeseed oil

Rapeseed oil, used for experiments was obtained from a local market and met the requirements of edible oil. The fatty acid composition of the rapeseed oil were determined according to the requirements of ISO 5508 standards. As heterogeneous catalyst the dolomite, produced by local company JSC Dolomitas was used. The characteristics of the catalyst were described in our others articles [6,8]. Dolomite were prepared according Gaide et al. who analyzed optimum conditions for dolomite preparation for oil transesterification [9]. First of all, dolomite were crushed and heated in a muffle furnace (AB UMEGA SNOL 8.2/1100) for 4 h at 850 °C. After calcination, the material was sieved. Particles were assumed to be in 0.1–0.315 mm range that was logarithmically divided into 5 PSD fractions which were populated by normal distribution function. Catalyst was supplied into mixture at 52.4 kg/h consisting of 60.5 % CaO (CAO) and 39.5 % MgO (MGO). Transesterification experiments were performed in the laboratory reactors connected to reflux condensers and containing heating and stirring equipment. The required amount of oil was poured into the reactor, the catalyst was added, and after heating the mixture to the required temperature while stirring at 250 rpm, the required amount of butanol (99.5 %, Chempur) was added. Post-reaction, the mixture was filtered to remove the catalyst and heated to remove excess of butanol. It was then washed with a 5 % H_3PO_4 solution (10 % of the reaction product's volume) and twice with distilled water (10 % of the mixture's volume). The remaining water was evaporated at 110 °C using a rotary evaporator.

2.2. Evaluation of ester yield and optimization of process

The ester yield was determined by quantifying the glycerides in the samples. Glycerol, monoglycerides, diglycerides, and triglycerides were analyzed using a Perkin Elmer Clarus 500 gas chromatograph (City, State Abbr., Country, detector—FID, column—Restek MXT-Biodiesel TG (0.15 m–0.32 mm–0.10 μm)) following the requirements of standard EN 14105.

Optimization of transesterification process was performed using Response Surface Methodology.

2.3. Modeling of transesterification

Physical modelling requires a lot of additional data about physical and chemical properties of materials so leading-in-class software Aspen Plus v12 was used to complete this task. Since analyzed heterogeneous transesterification includes solid catalyst, Aspen Plus software was the only option, since it has proprietary engine to calculate not only properties of solids themselves, but also solid-related processes. Process was designed using the equipment models presented in Table 1.

3. Results and discussions

3.1. Determination of optimal reaction conditions

The fatty acid composition of rapeseed oil are presented in Table 2. The optimal reaction conditions were determined by previous tests, the methods and results of which are described in article [8]. The catalyst – dolomite – was ground and sieved to a fraction of 0.315–0.1 mm before use and calcined at 850 °C. The transesterification process is influenced by numerous parameters, including oil acidity, water content, alcohol type and concentration, catalyst type, reaction temperature, duration, and mixing intensity [25]. In our study, we focused on investigating how four key variables affect this process (temperature,catalyst amount, molar ratio of butanol to oil, reaction duration). The transesterification reaction was carried out under different conditions, varying the values of the parameters listed above: temperature (from 6 to 117 °C), amount

Table 1
Block simulation and input specifications.

Process	Block	Input specification	Conditions
Tanks	Heater	Temperature and pressure	Pressure 1 atm, Temperature 20 °C
Pumps	Pump	Discharge pressure	Pressure 1–1.1 atm
Mixers	Mixer	Temperature and pressure	Pressure 1 atm, Temperature 20 °C
Reactor	RCSTR	Kinetic data	Pressure 1 atm, Temperature 80–110 °C
Filtering	CfFilter	Geometry (capillary diameter, length and number)	Pressure 1 atm, Temperature 80–110 °C
Distillation columns	RadFrac	Distillate rate, reflux ratio, condenser temperature	Pressure 0.1–1 atm, Temperature up to 284 °C
Decanter	Decanter	Temperature and pressure	Pressure 1 atm, Temperature 20 °C
Washers	Extract	Pressure and key components in separate phases	Pressure 1 atm

Table 2
Fatty acid composition of rapeseed oil.

Fatty acid	Value, %
Saturated fatty acids	
Butyric acid (C4:0)	0.04 ± 0.001
Caproic acid (C6:0)	0.13 ± 0.01
Caprylic acid (C8:0)	0.40 ± 0.03
Capric acid (C10:0)	1.97 ± 0.07
Undecylic acid (C11:0)	0.04 ± 0.002
Lauric acid (C12:0)	0.04 ± 0.003
Tridecanoic acid (C13:0)	1.29 ± 0.15
Myristic acid (C14:0)	0.05 ± 0.005
Pentadecanoic acid (C15:0)	0.02 ± 0.002
Palmitic acid (C16:0)	4.01 ± 0.11
Margaric acid (C17:0)	0.05 ± 0.01
Stearic acid (C18:0)	1.58 ± 0.16
Arachidic acid (C20:0)	0.59 ± 0.026
Heneicosylic acid (C21:0)	0.04 ± 0.001
Behenic acid (C22:0)	0.32 ± 0.05
Tricosylic acid (C23:0)	0.02 ± 0.005
Lignoceric acid (C24:0)	0.13 ± 0.01
Unsaturated fatty acids,	
Palmitoleic acid (C16:1 cis-9)	0.18 ± 0.02
Heptadecenoic acid (C17:1 cis-10)	0.06 ± 0.001
Oleic acid (C18:1)	59.95 ± 1.11
Linoleic acid (C18:2)	18.55 ± 0.95
Linolenic acid (C18:3)	8.86 ± 0.51
Paullinic acid (C20:1)	1.24 ± 0.03
Dihomo-gamma-linolenic acid (C20:3 8,11,14)	0.04 ± 0.002
Eicosatrienoic acid (C20:3 11,14,17)	0.05 ± 0.01
Erucic acid (C22:1)	0.15 ± 0.01
Brassic acid (C22:2)	0.02 ± 0.001
Docosahexaenoic acid (C22:6)	0.01 ± 0.33
Nervonic acid (C24:1)	0.15 ± 0.05

(from 4 to 10 wt%), the methanol-to-oil molar ratio (mol:mol) (from 4 to 16), the catalyst and the reaction duration (from 4 to 10 h). The highest ester yield of 95.9 % was obtained at 110 °C temperature using 5.2 % of dolomite as catalyst and 13.72 M ratio of butanol to oil at 8 h duration of process [8].

For further kinetics studies and modelling the determined optimal conditions were used.

3.2. Kinetics of transesterification

There are little data about kinetics of heterogeneous oil transesterification. Most of the scientific research is performed by alkali-catalyzed homogeneous transesterification of oils so mechanisms are almost fully understood. Despite being considerably faster and little limited by mass transfer, homogeneous transesterification has a number of disadvantages including high amounts of washing wastewater, non-reusable catalyst and low purity products. That is a primary reason why heterogeneous transesterification of oils gained popularity among scientists and various naturally occurring catalyst are used for production of biodiesel. The main downside of utilizing heterogeneous catalysts is the introduction of catalytically active centers that are in a separate phase between already immiscible reactants. This creates additional elementary steps of mass transfer to already quite complex process. The highest number of elementary steps can be attributed to the transesterification process with ion-resin acting as catalyst. This process follows Langmuir-Hinshelwood mechanism were both oil and alcohol must adsorb on active sits of catalyst first and only then hydrolysis and transesterification of glycerides can occur. Application of calcium-based catalysts showed, that reactions followed Eley-Rideal mechanism and only alcohol adsorbs with formation of alkoxides, while glycerides react from the liquid phase. This simplified mechanism lessens the influence of mass transfer on overall process rate and limiting step becomes reaction itself.

$$TG + 3ButOH = 3FABE + GLYCEROL \quad (1)$$

here: *TG* – triglyceride; *ButOH* – butanol; *FABE* – fatty acid butyl ester; *GLYCEROL* – glycerol.

It is established, that overall this reaction is the fourth order. In this study, molar ration between glycerides and butanol is 13.72, so concentration change of butanol during transesterification is negligible and has little influence on overall reaction rate. Since butanol is not used often as esterification agent in research, most widely used kinetic models were applied to the experimental data – irreversible and reversible pseudo-first order models.

For irreversible pseudo-first order reaction, kinetic equation can be written as follows:

$$-r = kC_{TG} \quad (2)$$

here: r – reaction rate; k – reaction rate constant; C_{TG} – concentration of triglyceride.

Since reaction rate is proportional to the concentration change of triglycerides and it can be represented by conversion degree, equation can be rewritten:

$$C_{TG} = C_{TG_0}(1 - \propto) \quad (3)$$

$$\frac{d\propto}{dt} = k(1 - \propto) \quad (4)$$

here: α – conversion degree.

Integrated form of irreversible pseudo-first order kinetic equation can be written as:

$$-\ln(1 - \propto) = kt \quad (5)$$

In reversible pseudo-first order reaction rate depends on the opposite forward and reverse reactions:

$$-r = k_{for}C_{TG} - k_{rev}C_{FABE} \quad (6)$$

here: k_{for} – reaction rate constant for forward reaction; k_{rev} – reaction rate constant for reverse reaction.

Concentration of FABE is proportional to the reacted amount of triglycerides, so equation becomes:

$$-r = k_{for}C_{TG} - k_{rev}C_{TG_0}\propto \quad (7)$$

When substituted just with conversion degrees, equation can be written:

$$\frac{d\propto}{dt} = k_{for}(1 - \propto) - k_{rev}\propto = k_{for}\left((1 - \propto) - \frac{\propto}{K}\right) \quad (8)$$

where K is an equilibrium constant of transesterification, which can be calculated when conversion degree reaches its equilibrium value:

$$K = \frac{\alpha_{eq}}{1 - \alpha_{eq}} \quad (9)$$

here: K – equilibrium constant of transesterification; α_{eq} – equilibrium conversion degree.

Final differential form of kinetic equation for reversible pseudo-first order reaction:

$$\frac{d\alpha}{dt} = k\left(1 - \frac{\alpha}{\alpha_{eq}}\right) \quad (10)$$

And the integrated form of equation:

$$-\ln\left(1 - \frac{\alpha}{\alpha_{eq}}\right) = kt \quad (11)$$

Kinetic experiments were performed in the span of 8 h with the previously established best ANOVA solution. In order to obtain a broader understanding about kinetics, transesterification reactions were performed at four different temperatures: 80, 90, 100, 110 °C and conversion degrees were calculated (Figs. 1 and 2).

Kinetic curves of transesterification indicate that conversion degree is highly dependent on the temperature. Even 10 degrees temperature difference has great impact on the rate of the process. During the duration of 8 h at 80 °C conversion of glycerides reached only 31.7 %. Just increasing temperature by 10 °C leads conversion degree going up by around 13 %. Each subsequent temperature increase increases conversion rate by a larger margin. This happens not only because of increasing intensity of transesterification reaction itself, but also because of decreasing viscosity of butanol, which is around two times higher than of methanol. Even the shapes of kinetic curves suggest that there might be mass transfer limitations in the process. It is recommended to perform this reaction at 110 °C when after 8 h degree of conversion reaches 90 %.

Kinetic modelling was performed by linear regression analysis using the most suitable kinetic equations for heterogeneously catalyzed transesterification – irreversible and reversible pseudo-first order models. It is very beneficial to establish whether reverse reaction has strong influence on reachable extent of conversion.

Reaction rate constants are calculated as slopes of presented straight lines and applicability of used models was assessed by calculating coefficients of determination. Obtained results are presented in Table 3.

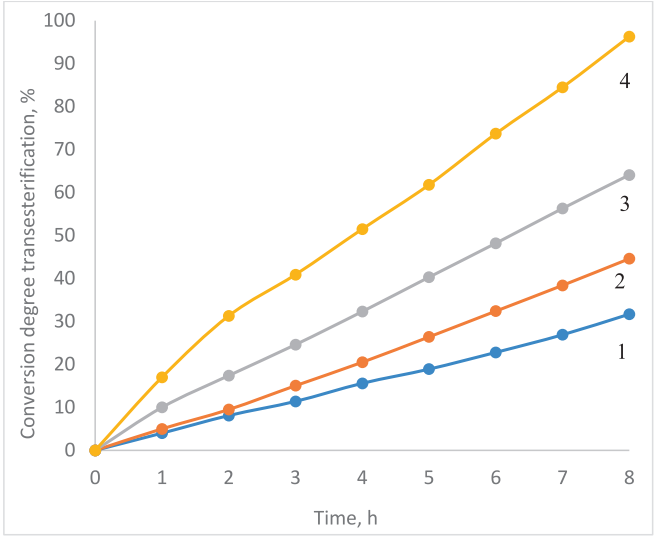

Fig. 1. Conversion degree of transesterification versus time obtained at different temperatures: 1 – 80 °C, 2 – 90 °C, 3 – 100 °C, 4 – 110 °C.

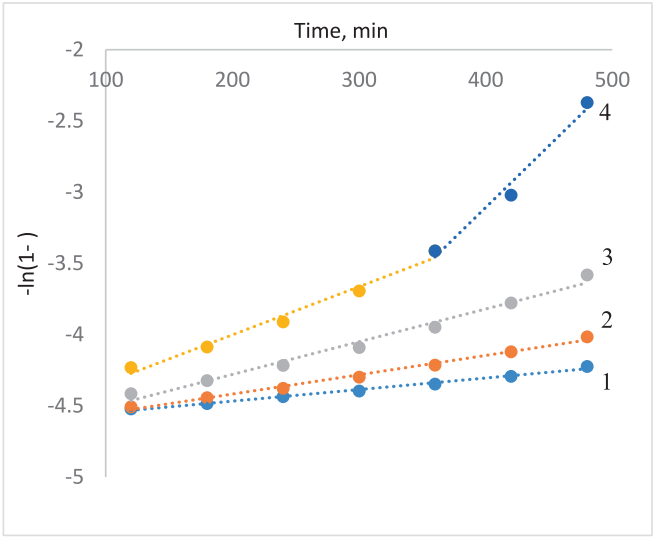

Fig. 2. . Kinetic curves of transesterification in irreversible pseudo-first order model coordinates at different temperatures: 1 – 80 °C, 2 – 90 °C, 3 – 100 °C, 4 – 110 °C.

Table 3
Kinetic parameters of oil transesterification with butanol.

Kinetic model	Linear form	Temperature, °C	k, min^{-1}	Coefficient of determination
Irreversible pseudo-first order	$-\ln(1-\alpha) = kt$	80	0.0008	0.9915
		90	0.0014	0.9915
		100	0.0023	0.9832
		110	0.0034	0.9825
Reversible pseudo-first order	$-\ln\left(1-\frac{\alpha}{\alpha_{eq}}\right) = kt$	80	0.0056	0.9653
		90	0.0055	0.9317
		100	0.0057	0.9293
		110	0.0057	0.9330

Applied kinetic models indicate, that forward reaction proceeds much faster than reverse and process is basically irreversible. The best fit of linear equations was observed for irreversible pseudo-first order model where coefficients of determination are higher than 98 %. Reversible pseudo-first order model fit experimental data worse, where coefficients of determination were at around 92–93 %.

Interesting observation can be made here, because coefficients for reversible model clearly decreases with the increasing temperature of the reaction. This might happen because of uneven change of reaction rate constants for forward and reverse reactions – equilibrium must be shifting towards FABE at higher temperatures. Even though irreversible pseudo-first order kinetic model fits experimental data very well – one peculiarity can be observed here also. At 110 °C when conversion degree reaches around 70 % the change of straight line slope is visible. This usually indicates that the limiting step in the complex process changes. In this case it is established, that initial step of transesterification is controlled by mass transfer and the latter one – by reaction itself. The data on diffusion and its activation energies is scarce, especially for transesterification reaction. It is even more difficult to find scientific data on butanolysis. But it is usually considered that diffusion activation energy is lower than reaction activation energy, and can be up to 40 kJ/mol. This means that reaction rate is more sensitive to temperature changes than diffusion. As Fig. 1 indicates, at the highest temperature when the larger part of viscous triolein reacts – reaction rate suddenly increases. This explains that there are no more mass transfer limitations as overall viscosity decreases and reaction rate can completely depend just on the remaining amounts of reactants. It is interesting, that transesterification with butanol is broadly limited by mass transfer, even

at 110 °C. Reaction at catalyst surface starts controlling the overall process only when conversion degree reaches 70 %. It explains peculiar form of kinetic curves.

Despite mass transfer limitations, calculated transesterification rate constants (Table 1) are similar to the ones reported by other researches. When compared to reactions with methanol, calculated reaction rate constants are a bit lower, for irreversible pseudo-first order ranges between 0.0008 and 0.0034 min^{-1}. Lukic et al [20] as well as Kaur and Ali [22] reported 10 times larger reaction rate constants depending on conditions, but of course they were determined for reactions with methanol. It is understandable, that butanolysis requires higher temperatures than methanolysis to achieve similar reaction rates. Reaction is clearly favoring increasing temperature, when reaction rate doubles with temperature increase increment of 10 °C.

Obtained reaction rate constant dependency on the temperature was used to determine activation energy of the reaction. For this Arrhenius equation was used:

$$k = Ae^{-\frac{E_a}{RT}} \tag{12}$$

here: k – reaction rate constant; A – Arrhenius constant; E_a – reaction activation energy; R – universal gas constant; T – temperature.

By applying logarithm to the equation, its linear form can be obtained and then it can be used for linear regression analysis.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{13}$$

When plotted in Arrhenius coordinates kinetic data gives straight line which slope can be used to determine activation energy of the reaction (Fig. 3).

Kinetic data fit Arrhenius equation very well and determined activation energy is 54451 J/mol. This result is comparable to the activation energies of methanolysis reported by other authors. Activation energy of 54.5 kJ/mol falls in to the middle of the range which was established by scientists – between 30 and 90 kJ/mol [26,27]. For heavily diffusion-controlled processes activation energy might get over 100 kJ/mol [19]. But if kinetics-controlled, both homogeneous and heterogeneous transesterifications seem to have the same range of varying E_a. Activation energy itself seems to depend on the alcohol which is used for transesterification. Kaur and Ali [22] noticed, that transesterification with ethanol on Zr/CaO heterogeneous catalyst requires more activation energy when compared to methanolysis. For ethanol activation energy was 42.5 kJ/mol, while for methanol 29.8 kJ/mol. It could be predicted, that for butanolysis it should be higher. The combination of steric hindrance, lower polarity, slower mass transfer, and slightly less favorable reaction energetics makes the reaction with butanol require a higher activation energy than with methanol or ethanol [28–30].

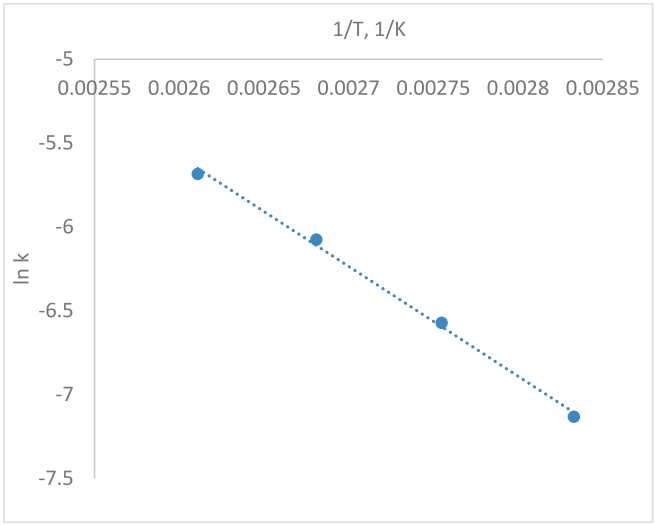

Fig. 3. Reaction rate constants in Arrhenius plot.

3.3. Modeling of transesterification in Aspen plus

The main aim of modelling of biodiesel production was to upscale laboratory equipment and techniques while the outcome of software calculations being similar to the obtained results in the laboratory. 1000 kg/h of rapeseed oil was used as a basis for calculations, which would require 1146 kg/h of butanol to complete transesterification at various durations and temperatures. Amount of butanol was calculated using optimized ratio of butanol to oil ratio 13.71:1. The main difficulty is to properly define rapeseed oil both physically and chemically, since it consists of thousands of different compounds of various classes with their unique thermodynamic properties and binary interactions. Therefore, typical simulation would include only the most common and abundant components to ensure that there is enough thermodynamic data and its calculations would be executable by software in limited number of iterations. For this reason, rapeseed oil was modelled as one common triglyceride – triolein. This compound is quite often used to model biodiesel production. Since catalyst (CAT) used is a solid, which has defined volume and particle size, particle size distribution (PSD) was also integrated in the solid-state model. Particles were assumed to be in 0.1–0.315 mm range that was logarithmically divided into 5 PSD fractions which were populated by normal distribution function. Catalyst was supplied into mixture at 52.4 kg/h consisting of 60.5 % CaO (CAO) and 39.5 % MgO (MGO).

The thermodynamic characteristics and attributes of the employed materials were assessed utilizing the NIST ThermoData Engine, supplemented by manual input for any absent data, because there is little information about interactions between glycerol (G), triolein (TG), butanol (BUT) and butyl oleate (FABE). To calculate the activities of compounds and gauge their phase equilibrium and binary interactions in the non-ideal liquid phase, the NRTL (nonrandom two liquid) activity coefficient model was applied.

Considering the specific laboratory methodologies and equipment utilized in the conducted experimental trials, a schematic representation of the biodiesel production was formulated in the form of a flowsheet (Fig. 4).

1000 kg/h of rapeseed oil is supplied from the tank T2 with pump P2 and are mixed with solid CaO and MgO catalyst At the same time butanol are supplied from tank T1 with pump P1. Both flows are preheated to desired reaction temperature in heaters HEAT1 and HEAT2, mixed together and directed to the reactor REACTOR, which operates isothermally. Transesterification proceeds with rate-controlled reaction on catalyst that can be written as:

$$TG + 3ButOH + CAT = 3FABE + GLYCEROL + CAT \tag{14}$$

here: CAT – catalyst.

Since solid catalyst participates in the reaction, initial step after reaction is to filter them out in FILTER. Permeate is the supplied to column COL1, to separate alcohol from the rest of mixture. After separation of butanol remaining mixture is then split into two phases in DECANTER. The lighter top phase consisting of biodiesel and oil is washed with water in washers WASH1 and WASH2 keeping the amount of water 1/10 of the product. Since biodiesel has still impurities of oil and alcohol, second distillation is needed in COL2. Column operates with partial condenser to additionally separate butanol from biodiesel and obtain better quality product. Remaining oil is collected at the bottom of the column.

The heavier phase from decanter contains glycerol which can be additionally purified to receive crude or technical grade glycerol. Bottom phase of decanter is supplied to distillation column COL3 which separates butanol from glycerol.

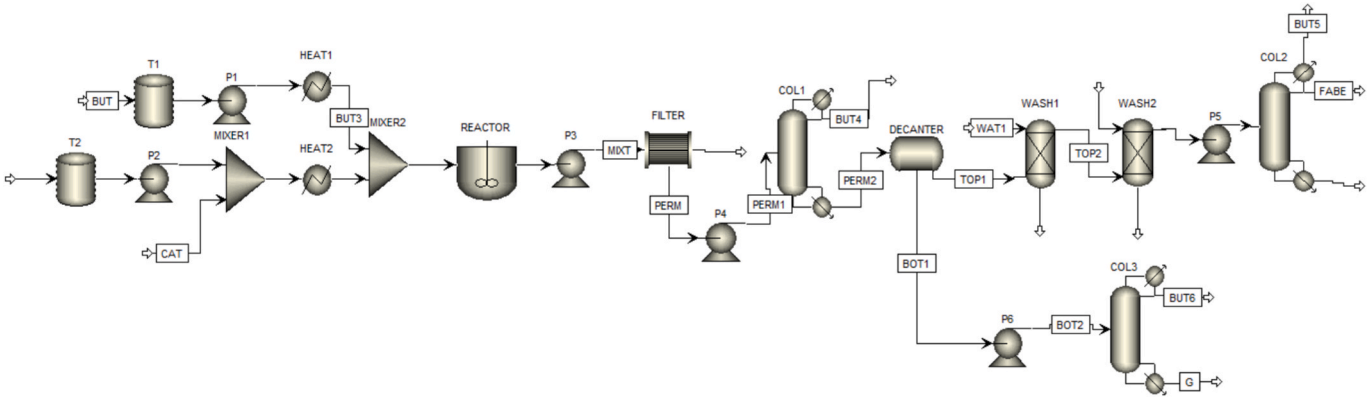

Fig. 4. Heterogeneous transesterification of rapeseed oil model in Aspen Plus.

Considering previous kinetic calculations, experimental results were modelled in relation to time and temperature. Because viscosity and diffusive limitations of reactive mixture has a great impact on the reaction rate, apparent order of reaction was assumed to be zero, because kinetic curves appear to be similar to straight lines. Comparison of experimental results and Aspen Plus calculations are presented in Fig. 5.

The alignment between both models in the figure is evident, suggesting a high degree of concordance. Consequently, the Aspen Plus model stands as a reliable independent tool for upscaling production, selecting the requisite equipment, and conducting energy-saving analyses. Aspen Plus calculations affirm that to attain the highest yield of biodiesel 110 °C temperature and 8 h of residence time is needed. At the same time sensitivity analysis of reactor was performed plotting two variables – residence time and temperature against formed FABE amount. 3D plot of sensitivity analysis shows strong influence of both variables with surface of data being steeply curved at high temperatures and long residence times.

Considering different process conditions, the reaction volume for 1000 kg/h of oil fluctuates between 2.672 and 2.756 m^3/h depending on the temperature. Having in mind, that residence time of reactants should be 8 h, the needed reactor volume ranges between 21.403 and 22.172 m^3. This implies that a 25 m^3 continuously stirred tank reactor would be adequately sufficient for implementing this process. Mass balance at 110 °C and 8 h of residence time is presented in Table 4.

The dimensions and quantity of the solid catalyst remain constant regardless of the conditions, and the amount is relatively small. Therefore, the filter was simulated as a capillary filter, due to the insufficient quantity of solids for disk, plate, or drum separators. For simulated process the aim was to implement filters whose dimensions would be around couple meters in size. For these two sections of two capillaries would do the work, each one 1 m in diameter and 3 m in length. Average fluid velocity should be 0.5 m/s with specific filtration rate 0.0731 m^3/(m^2 h).

Permeate, devoid of solids, can undergo further separation. However, due to butanol's strong solubility in diesel, a distillation column is employed initially instead of a decanter. This approach is particularly cost-effective since the reactor operates at elevated temperatures, requiring a relatively modest increase in temperature therefore reducing energy consumption. Since boiling point of butanol is very different from rest of components small reflux ratio of 0.1 was used together with 5 equilibrium calculated stages with total condenser. Optimal duty of reboiler was determined using sensitivity analysis and plotting distillate rate against reboiler duty. Received results are presented in Fig. 6.

Distillation column should completely remove butanol from product mixture, but curve become very steep, when draw rate of distillate becomes more than 800 kg/h. In this case additional 100 kg/h of distillate requires approximately 1.5 times more energy for reboiler, which might not be beneficial economically. Considering additional column for purification of FABE will be needed either way, remaining butanol can be removed later. At 800 kg/h of distillate rate, reboiler would need 212 kW, which is quite comparable to other Aspen modelling results, which

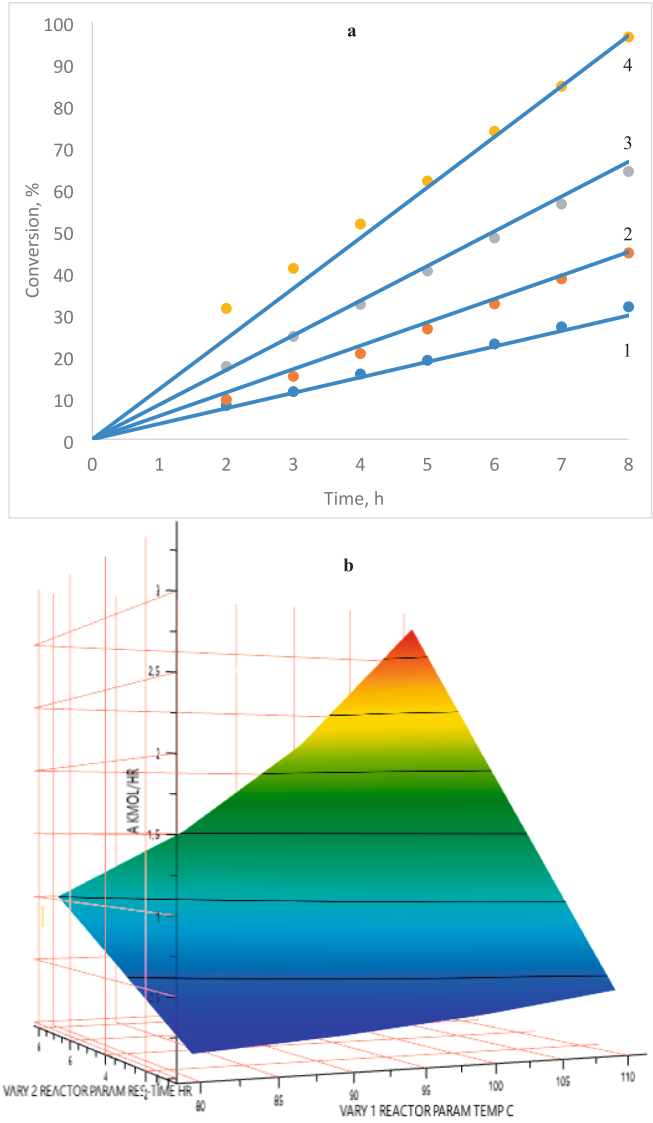

Fig. 5. Comparison (a) of experimental results (dots) and Aspen Plus (lines) rate-based modelling at various temperatures: 1 – 80 °C; 2 – 90 °C; 3 – 100 °C; 4 – 110 °C and sensitivity analysis 3D plot (b).

Table 4
Stream results of reactor, operating at 8 h and 110 °C.

Ingoing		Outgoing	
Component	**kg/h**	**Component**	**kg/h**
TG	1000	TG	34.7
G	0	G	100.4
FABE	0	FABE	1107.3
BUT	1146	BUT	903.6
CAO	31.7	CAO	31.7
MGO	20.7	MGO	20.7
Total	**2198.4**	**Total**	**2198.4**

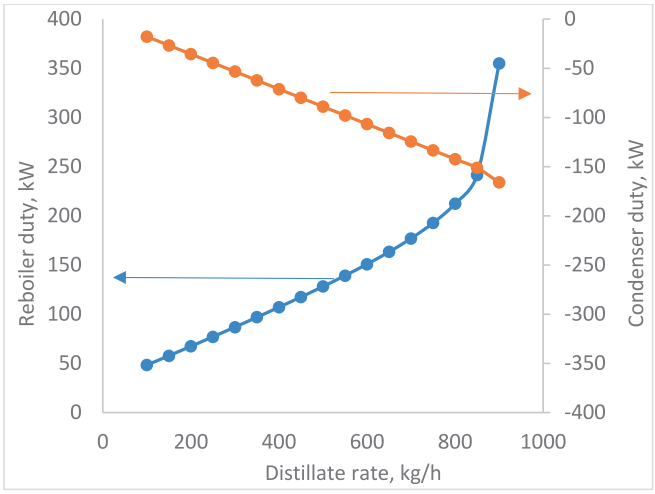

Fig. 6. Reboiler and condenser duty dependence on distillate draw rate for butanol distillation at reflux = 0.1.

ranges between 200 and 250 kW for reboiler in atmospheric distillation [17,31]. Boon-anuwat et al compared energy consumption for various setups of distillation and conventional distillation required largest amount of energy 260 kW [17]. Vacuum distillation could reduce energy consumption for reboiler around three times, but only for homogeneous transesterification. For heterogeneous transesterification vacuum distillation has similar energy consumption as conventional. In order to minimize energy consumption, condenser can be utilized as a source of heat, which would supply 142 kW of condensation energy.

But other models investigate transesterification with methanol, which requires lower temperature for distillation therefore, lower energy consumption. In the case of butanol transesterification, reaction proceeds at much higher temperature than methanol transesterification, so increase in energy consumption for distillation is not evident.

Composition profile of the column indicates how well internals of column are utilized. Larger number of equilibrium stages yields softer transition of temperatures. Fig. 7 indicates that 3 or 4 stages are sufficient enough for butanol removal, because composition and temperature in the first 2 top stages does not change. Therefore, smaller column can be utilized for butanol distillation. After removal of large excess of butanol, glycerol can be separated from the rest of the mixture in a decanter taking into advantage large differences in density of components. Decanter operates at 20 °C and lighter phase of TG and FABE is separated from heavier phase of glycerol. Due to its considerable solubility in both phases, a greater proportion of butanol persists in diesel, whereas only a fifth is extracted along with glycerol. This occurs because the flow of FABE is approximately ten times greater than that of glycerol. The purification of FABE requires an additional processing step, which involves the removal of glycerol and butanol impurities. This purification process takes place in two extractors connected in sequence, each receiving a continuous supply of 60 kg/h of water. The water volume required for washing is determined as 10 % of the total FABE quantity. Although this water effectively eliminates glycerol from the diesel, a notable amount of butanol, along with unreacted oil, still persists in the mixture. As a result, further distillation of the diesel is necessary.

Diesel distillation is also modelled as a column consisting of 5 equilibrium stages. Since boiling points of FABE and TG are not that different, larger reflux ration of 1 was used to model distillation. At the same time because of diesel sensitivity to high temperatures, vacuum distillation was considered at 0.1 bar absolute pressure. Since butanol has the lowest boiling point, it easily distills together with FABE. In this case partial condenser is used to additionally separate FABE from butanol. Sensitivity analysis (Fig. 8) indicates, that reboiler duty directly depends on the rate of distillate so in this case draw rate was considered to be 1100 kg/h, leaving only few percent of FABE in the remaining oil. As it was expected, energy consumption for diesel distillation is much higher. For distillate draw rate of 1100 kg/h, reboiler would require 453 kW. Composition and temperature profiles for diesel distillation are presented in Fig. 9.

Composition in the liquid phase of diesel distillation column shows, that there is little change in the stages between 2 and 4. But temperature profile suggests that temperature changes slightly, so column could be smaller by one stage. Temperature of partial condenser was selected depending on the purification degree of FABE and condenser duty

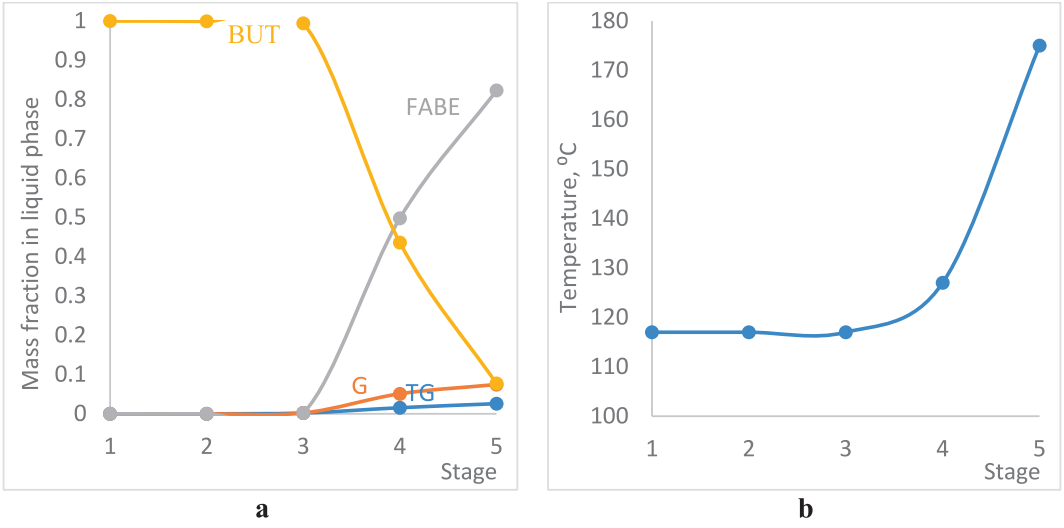

Fig. 7. Composition (a) and temperature (b) profiles of butanol distillation column through stages 1 to 5.

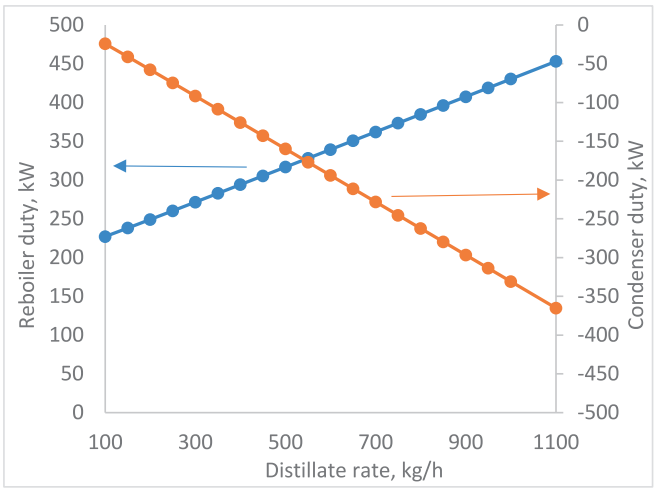

Fig. 8. Reboiler and condenser duty dependence on distillate draw rate for FABE distillation at reflux = 1.

(Fig. 10). The dependence of condenser duty on the condenser temperature follows a nearly linear trend. Therefore, the condenser temperature was set to 120 °C, resulting in a biodiesel ester content of approximately 98 wt%. This slightly exceeds the required minimum ester content of 96.5 wt% (see Fig. 11).

Technology of biodiesel production could also be used for production of glycerol. Depending on the equipment the received glycerol can be of crude (>85 wt%) or technical grade (>98 wt%).

Glycerol received from the bottom of decanter has lower concentration 71.2 wt%, so additional distillation column is needed to remove butanol. Boiling points of butanol and glycerol are very different, so 5 stage equilibrium column operates with reflux ratio of 0.1. Distillation column operates at absolute pressure of 0.1 bar. As sensitivity analysis indicates, maximum achievable grade of glycerol in this technology is a crude grade. Higher than 85 % glycerol can be obtained if 21 kg/h distillate draw rate is used. This would require around 15 kW for reboiler. Higher purity would increase energy requirements exponentially, so it might not be economically beneficial.

The overall energy consumption of the processes for transesterification of 1000 kg/h of oil at optimal conditions is presented in Table 5.

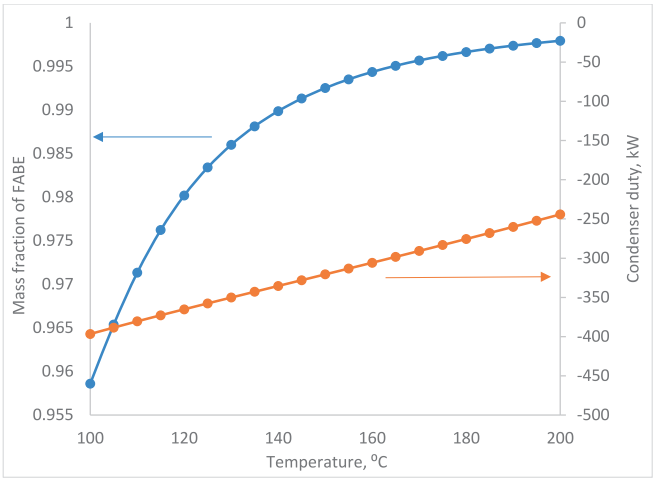

Fig. 10. Content of FABE in distillate and condenser duty depending on the temperature of partial condenser in diesel distillation column.

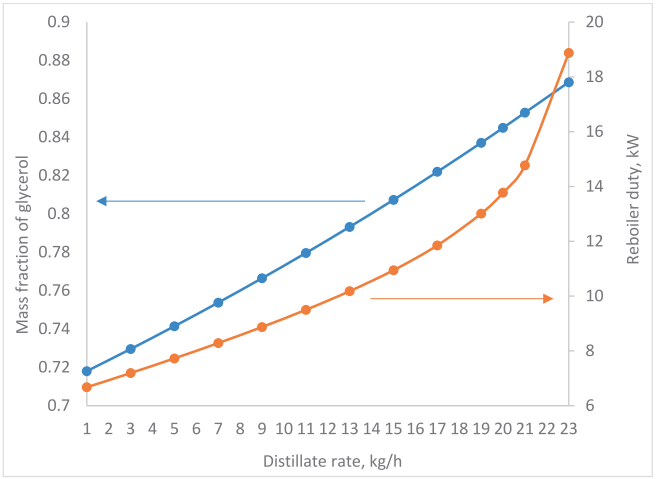

Fig. 11. Glycerol purity and reboiler duty dependence on the draw rate of distillate in the glycerol distillation column.

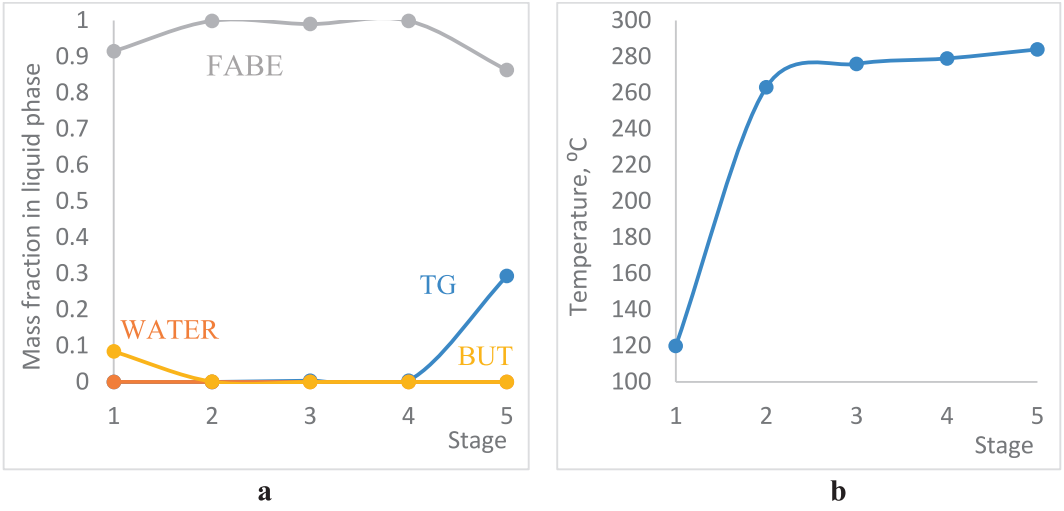

Fig. 9. Composition (a) and temperature (b) profiles of diesel distillation column through stages 1 to 5.

Table 5
Overall energy consumption of the processes at optimal conditions.

Process	Block	Notation	Duty
Butanol heating	Heater	HEAT1	89 kW
Rapeseed oil heating	Heater	HEAT2	48 kW
Butanol distillation column	RadFrac	COL1	Reboiler: 212 kW Condenser: −142 kW
Biodiesel distillation column	RadFrac	COL2	Reboiler: 453 kW Condenser: −365 kW
Glycerol distillation column	RadFrac	COL3	Reboiler: 15 kW Condenser: −4 kW

4. Conclusions

Kinetic experiments of heterogeneous transesterification at determined optimal conditions using dolomite as catalyst indicated that transesterification proceeds as irreversible pseudo-first order reaction with observable mass transfer limitations at temperatures lower than 110 °C. Reaction rate increases with increasing temperature and kinetic data fit Arrhenius equation very well. Determined activation energy was 54451 J/mol which is comparable to the activation energies of methanolysis. Kinetic data was used to model and simulate continuous reactor calculated for 1000 kg/h of rapeseed oil. Applied kinetic data gave accurate fit in the analyzed ranges of time and temperature. For transesterification of 1000 kg/h of rapeseed oil at 8 h of residence time, 25 m^3 continuously stirred tank reactor would produce enough biodiesel reaching the desired conversion. After two steps of washing as well as distillation of butanol and biodiesel, 98 wt% purity product will be received which is up to EN 14214 requirements.

Duty requirements for reboilers of butanol and biodiesel distillation columns are a bit higher when compared to methanolysis process and are 212 kW and 453 kW respectively. Technology might implement additional purification step to receive additional product – glycerol. Modeling of glycerol distillation indicated, that crude grade glycerol (>85 %) is achievable with reboiler duty of 15 kW.

CRediT authorship contribution statement

Ieva Gaidė: Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andrius Jaskūnas:** Writing – original draft, Visualization, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Violeta Makarevičienė:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Eglė Sendžikienė:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Investigation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.

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