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Influence of Mass Transfer and Kinetics on Biodiesel Production Process

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1. Introduction

Biodiesel is produced by the transesterification of large branched triglycerides (TG) (usually vegetable oils) into smaller, generally straight-chain molecules of alkyl (most often methyl) esters in the presence of a catalyst. Di- and monoglycerides (DG and MG) are intermediates and glycerol (G) is the side product. The three reactions are consecutive and reversible.

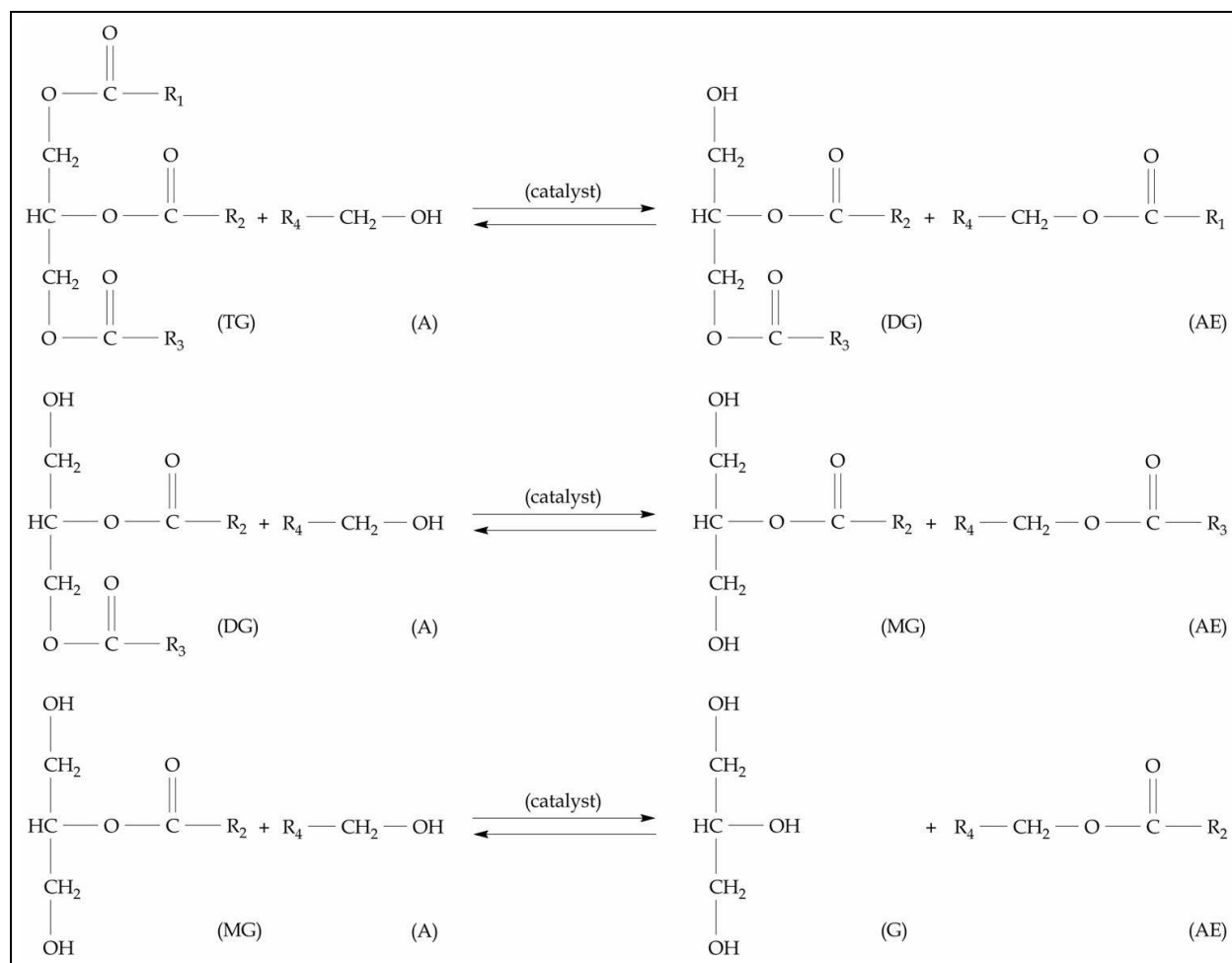


Fig. 1. Reaction scheme of triglyceride transesterification to glycerol and alkyl ester

2. Mass transfer-determined rate of biodiesel production process

2.1 Batch reactors

The reaction system in a batch reactor may be considered as a pseudo-homogeneous one with no mass transfer limitations (Marjanovic et al., 2010). Nonetheless, a reaction mechanism consisting of an initial mass transfer-controlled region followed by a kinetically controlled region is generally proposed (Noureddini & Zhu, 1997). Recently, there is an increased interest in new technologies related to mass transfer enhancement (Leung et al., 2010). Biodiesel production process may be catalyzed by acids and bases, and these influence mass transfer in a batch reactor. Lewis acid catalysts are active for both esterification and transesterification, but the reaction is very slow due to mass transfer limitations between methanol and oil phase (Hou et al., 2007). Experiments may be conducted at ambient temperature to study mass transfer limitations, indicated by the presence of a triglyceride induction period, during the acid-catalyzed transesterification reaction (Ataya et al., 2008b). The immiscibility of methanol and vegetable oil leads to a mass transfer resistance in the transesterification of vegetable oil (Guan et al., 2009). Likewise, the use of meso-structured supports is shown as a factor improving the catalytic performance as compared with macro-porous sulfonic acid-based resins, likely due to an enhancement of the mass transfer rates of large molecules, such as triglycerides, within the catalyst structure (Melero et al., 2010). However, acid exchange resins deactivation in the esterification of free fatty acids is always present in the system (Tesser et al., 2010).

The conventional base-catalyzed transesterification is characterized by slow reaction rates at both initial and final reaction stages limited by mass transfer between polar methanol/glycerol phase and non-polar oil phase (Zhang et al., 2009). If using specific catalysts, the homogeneous single phase is formed at 3:1 methanol to oil molar ratio and the mass transfer resistance between the methanol/triglyceride phases disappears (Tsuji et al., 2009). However, the methanol in the system is not effectively used for the reaction due to interface mass transfer resistance (Kai et al., 2010). Meanwhile, the process model indicates that the transesterification reaction is controlled by both mass transfer and reaction (Liu et al., 2010). Transesterification was performed in a 30 L reactor by Sengo et al. (2010), under previously optimized conditions and a yield of 88% fatty acid methyl esters was obtained after 90 min of reaction time, due to mass transfer limitations. Thus, the transesterification reaction is initially mass transfer-limited because the two reactants are immiscible with each other, and later because the glycerol phase separates together with most of the catalyst (sodium or potassium methoxide) (Cintas et al., 2010).

The sigmoid kinetics of the process is explained by the mass transfer controlled region in the initial heterogeneous regime, followed by the chemical reaction-controlled region in the pseudo-homogeneous regime. The mass transfer is related to the drop size of the dispersed (methanol) phase, which reduces rapidly with the progress of the methanolysis reaction (Stamenkovic et al., 2008). It is observed that droplet size has a major influence on reaction end point and that the reaction is mass transfer-limited. This observation is confirmed by developing a mass transfer-based reaction model using the data from the batch reactor which agrees with results from other researchers (Slinn & Kendall, 2009). Biodiesel fuel yields increase with the addition of sodium dodecyl sulfonate as surface active agent because the mass transfer rates of protons and methanol to the oil phase through the oil-methanol interface are increased with increasing interfacial area (Furukawa et al., 2010). Analogously may be reasoned when a solid catalyst is present in the process. The sigmoid process kinetics is explained by the initial triglyceride mass transfer controlled region, followed by the chemical reaction controlled region in the latter reaction period. The

triglyceride mass transfer limitation is due to the small available active specific catalyst surface, which is mainly covered by adsorbed molecules of methanol. In the later phase, the adsorbed methanol concentration decreases, causing the increase of both the available active specific catalyst surface and the triglyceride mass transfer rate, and the chemical reaction rate becomes smaller than the triglyceride mass transfer rate (Veljkovic et al., 2009). A kinetic model can also be expressed as three significant controlled regions, i.e., a mass transfer-controlled region in the internal surface of a heterogeneous catalyst, an irreversible chemical reaction-controlled region in the pseudo-homogenous fluid body and a reversible equilibrium chemical reaction-controlled region near to the transesterification equilibrium stage (Huang et al., 2009). The methanolysis process using calcium hydroxide catalyst is also shown to involve the initial triglyceride mass transfer-controlled region, followed by the chemical reaction controlled region in the later period. The triglyceride mass transfer limitation is caused by the low available active specific catalyst surface due to the high adsorbed methanol concentration. Both the triglyceride mass transfer and chemical reaction rates increase with increasing the catalyst amount (Stamenkovic et al., 2010).

Influence of mass transfer on the production of biodiesel may be observed through mixing variation as the use of different mixing methods (magnetic stirrer, ultrasound and ultraturrax) results in different conversions for the transesterification of rape oil with methanol in both acidic and basic systems (Lifka & Ondruschka, 2004a; Lifka & Ondruschka, 2004b). A reaction mechanism for sunflower oil is proposed involving an initial region of mass transfer control followed by a second region of kinetic control. The initial mass transfer-controlled region is not significant using 600 rpm (Vicente et al., 2005). The mechanism of *Brassica carinata* oil methanolysis also involves an initial stage of mass transfer control, followed by a second region of kinetic control. However, the initial mass transfer-controlled step is negligible using an impeller speed of at least 600 rpm (Vicente et al., 2006). In the case of crude sunflower oil, mass transfer limitation is effectively minimized at agitation speeds of 400–600 rpm with no apparent lag period (Bambase et al., 2007).

Optimization of mechanical agitation and evaluation of the mass transfer resistance is essential in the oil transesterification reaction for biodiesel production. The KOH-catalyzed transesterification of sunflower oil with methanol was studied by Frascari et al. (2009) in batch conditions in a 22 L stirred reactor in order to develop criteria for the energetic optimization of mechanical agitation in the biodiesel synthesis reaction, obtain preliminary information on the decantation of the reaction products, and evaluate the influence of the mass transfer resistance under different mixing conditions. An evaluation of the reaction and mass transfer characteristic times shows that the optimized tests are characterized by a not negligible mass transfer resistance (Frascari et al., 2009).

The tests conducted with one single static mixer at a 1.3 m/s superficial velocity (Reynolds number, $Re = 1490$) result in a profile of sunflower oil conversion versus time equivalent to that obtained in the best-performing test with mechanical agitation, indicating the attainment of a reaction run not affected by mass transfer limitations. In an evaluation of the energy requirement for the attainment of the alcohol/oil dispersion, the static mixer tests perform better than those with mechanical agitation (17 vs. 35 J/kg of biodiesel, in the reaction conditions without mass transfer constraints) (Frascari et al., 2008).

In the case of increasing ultrasound intensity, the observed mass transfer and kinetic rate enhancements are due to the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz are applied to a two-phase reaction system (Colucci et al., 2005). The high yield under the ultrasonic irradiation condition is due to high speed mixing and mass transfer between the methanol and triolein

as well as the formation of a micro-emulsion resulting from the ultrasonic cavitation phenomenon (Hanh et al., 2008). Cavitation results in conditions of turbulence and liquid circulation in the reactor which can aid in eliminating mass transfer resistances. The cavitation may be used for intensification of biodiesel synthesis (esterification) reaction, which is mass transfer-limited reaction considering the immiscible nature of the reactants, i.e., fatty acids and alcohol (Kelkar et al., 2008). A certain degree of conversion attributed to heterogeneity of the system, which adds to mass transfer resistances under conventional approach, appears to get eliminated due to ultrasound (Deshmane et al., 2009). The high yield for the crude cottonseed oil biodiesel under the ultrasonic irradiation condition is also attributed to the efficacy of cavitation, which can enhance the mass transfer between the methanol and crude cottonseed oil (Fan et al., 2010).

At three temperatures studied by Stamenkovic et al. (2008), the mass transfer coefficients of triglycerides into alcohol phase (at good confidence interval values) ranged from $1.40 (\pm 0.01) \times 10^{-7}$ to $1.45 (\pm 0.01) \times 10^{-6} \text{ m s}^{-1}$, consistent with the reported literature values of approximately 10^{-7} – 10^{-3} m s^{-1} (Frasdari et al., 2009; Klofutar et al., 2010). From these values, the specific activation energies of first-order triglyceride mass transfer (E_a) were estimated, and again a good fit was obtained. Table 1 shows the (average) values of the mass transfer coefficients at different reaction temperatures. Also, it has to be noted that in Table 1 the mass transfer coefficient values using the mixing rate of 700 min^{-1} are 10.3-times higher than those reported in the literature using mechanical agitation of 100 min^{-1} . This data was used to determine the activation energy of the mass transfer coefficients. The estimated mass transfer coefficients for sunflower oil and KOH catalyst reported in the literature (Frasdari et al., 2009; Klofutar et al., 2010) were compared at similar mixing rates. Lower mass transfer coefficients were reported for lower temperatures, since the mass transfer coefficients obtained by Frasdari et al. (2009) at 60°C were greater than that obtained by Klofutar et al. (2010) at 40°C and 50°C . The mass transfer coefficient (k_c) determined by Ataya et al. (2007) was much lower than that reported in the other literature. In the case of Liu et al. (2010), the apparent mass transfer coefficient value is not representative of the maximal coefficient that can be reached by reacting molecules before the reaction will occur, since the determination of mass transfer parameters was performed without acknowledging the experimental regime and the coefficient was consequentially unusually high.

Table 2 shows the calculated effective activation energies and pre-exponential factors of mass transfer coefficients (E_a and k_{c0}) for different reaction conditions and the corresponding literature sources. Similar activation energy values were obtained for the methanolysis of sunflower oil regardless of different impeller speeds (Stamenkovic et al., 2008; Klofutar et al., 2010). The disagreement was quite small in both cases, and as a result, the proposed mass transfer model adequately described the results from the experiments. The value of E_a , corresponding to the mass transfer in the case of the reactions of canola oil, was much lower and was considered to indicate less temperature-dependent behaviour of the coefficient. In this sense, the mass transfer of triglycerides to alcohol phase to give diglycerides, monoglycerides and glycerol is not much more favourable upon temperature increase, because of the poorer miscibility of canola oil-originating triglycerides and alcohol, which consequently involves comparably greater mass transfer resistance in the direction of alcohol phase at high temperatures in the case of canola oil than in the case of sunflower oil. Consequently, the mass transfer step (the mass transfer of triglyceride into alcohol) may be considered rate-determining for higher temperatures in the case of canola oil in comparison to sunflower oil. According to the k_c values at higher temperatures (50°C), the mass transfer from triglyceride phase to alcohol phase was slower for canola oil than for sunflower oil.

| Reaction temperature /°C | N /min ⁻¹ | k _c or k _c a | Oil | Catalyst | Literature |
|--------------------------|----------------------|--|---------------------|------------------------------------|----------------------------|
| 20 | 500 | $7.28 \times 10^{-7} \text{ s}^{-1}$ | Canola | H ₂ SO ₄ | (Ataya et al., 2007) |
| 10 | 200 | $1.45 \times 10^{-7} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 20 | 200 | $3.02 \times 10^{-7} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 30 | 200 | $1.45 \times 10^{-6} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 10 | 200 | $1.40 \times 10^{-7} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 20 | 200 | $3.02 \times 10^{-7} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 30 | 200 | $1.30 \times 10^{-6} \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 45 | Variable | $1.67 \times 10^{-7} \text{ s}^{-1}$ | Palm | Lipase | (Al-zuhair et al., 2009) |
| 60 | 100 | $5.30 \times 10^{-5} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 60 | 200 | $1.20 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 60 | 250 | $1.60 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 60 | 300 | $2.00 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 60 | 400 | $2.80 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 60 | 700 | $5.50 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower | KOH | (Frasconi et al., 2009) |
| 40 | 500 | $4.00 \times 10^{-6} \text{ m s}^{-1}$ | Sunflower | KOH | (Klofutar et al., 2010) |
| 50 | 500 | $1.70 \times 10^{-5} \text{ m s}^{-1}$ | Sunflower | KOH | (Klofutar et al., 2010) |
| 40 | 500 | $6.92 \times 10^{-6} \text{ m s}^{-1}$ | Canola | KOH | (Klofutar et al., 2010) |
| 50 | 500 | $1.18 \times 10^{-5} \text{ m s}^{-1}$ | Canola | KOH | (Klofutar et al., 2010) |
| 40 | 500 | $7.83 \times 10^{-5} \text{ m s}^{-1}$ | Sunflower Canola | KOH | (Klofutar et al., 2010) |
| 50 | 500 | $2.04 \times 10^{-4} \text{ m s}^{-1}$ | Sunflower Canola | KOH | (Klofutar et al., 2010) |
| 65 | 900 | $1.15 \times 10^{-1} \text{ m s}^{-1}$ | Soybean | Ca(OCH ₃) ₂ | (Liu et al., 2010) |

Table 1. Mass transfer parameters for the triglyceride transesterification reaction

| N /min ⁻¹ | C _c /wt. % | E _a /kJ mol ⁻¹ | k _{c0} /m s ⁻¹ | Oil | Catalyst | Literature |
|----------------------|-----------------------|--------------------------------------|--|---------------------|----------|----------------------------|
| 200 | 1 | 81.8 | $1.54 \times 10^8 \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 200 | 1 | 79.2 | $5.06 \times 10^7 \text{ m s}^{-1}$ | Sunflower | KOH | (Stamenkovic et al., 2008) |
| 500 | 1 | 121.7 | $8.10 \times 10^{12} \text{ m s}^{-1}$ | Sunflower | KOH | (Klofutar et al., 2010) |
| 500 | 1 | 45.2 | 2.38 m s^{-1} | Canola | KOH | (Klofutar et al., 2010) |
| 500 | 1 | 80.4 | $2.04 \times 10^7 \text{ m s}^{-1}$ | Sunflower Canola | KOH | (Klofutar et al., 2010) |

Table 2. Activation energies and pre-exponential factors of mass transfer coefficients

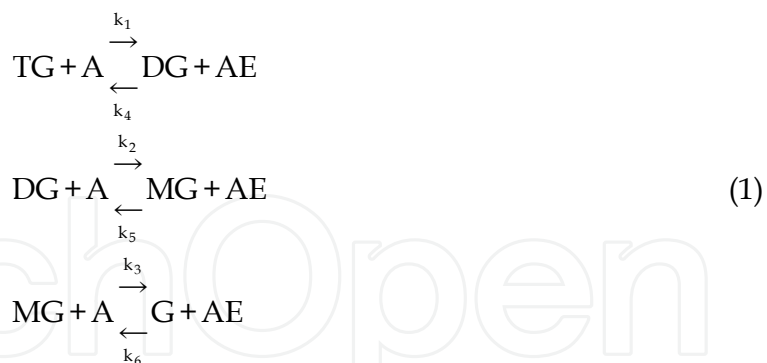
To study the effect of a solvent on mass transfer, experiments were performed by Ataya et al. (2006) at ambient temperature to investigate mass transfer during the transesterification reaction of canola oil with methanol (CH₃OH) to form fatty acid methyl esters by use of a sodium hydroxide (NaOH) base catalyst. Small conversions, at ambient conditions, accentuate the effects of mass transfer on the transesterification reaction. The influence of mass transfer is indicated by the increased reaction rate resulting from stirring a two-phase reaction mixture and changing a two-phase reaction to a single-phase reaction through the addition of a solvent (Ataya et al., 2006).

| Symbol | Value | Description and units | Literature |
|-------------------|---|---|-------------------------|
| [TG] | Variable | Triglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [TG] _i | [TG] _d /D or [TG] | Interface triglyceride concentration / kmol m ⁻³ | / |
| [TG] _d | ρ _{TG} /M _{TG} | Dispersed phase triglyceride concentration / kmol m ⁻³ | / |
| [DG] | Variable | Diglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [MG] | Variable | Monoglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [G] | Variable | Glycerol concentration in dispersed phase / kmol m ⁻³ | / |
| [A] | Variable | Alcohol concentration in dispersed phase / kmol m ⁻³ | / |
| [AE] | Variable | Alkyl ester concentration in dispersed phase / kmol m ⁻³ | / |
| [TG] ₀ | 0 | Initial triglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [DG] ₀ | 0 | Initial diglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [MG] ₀ | 0 | Initial monoglyceride concentration in dispersed phase / kmol m ⁻³ | / |
| [G] ₀ | 0 | Initial glycerol concentration in dispersed phase / kmol m ⁻³ | / |
| [A] ₀ | ρ _A /M _A | Initial alcohol concentration in dispersed phase / kmol m ⁻³ | / |
| [AE] ₀ | 0 | Initial alkyl ester concentration in dispersed phase / kmol m ⁻³ | / |
| M _{TG} | 871.55 | Triglyceride molecular mass / kg kmol ⁻¹ | (Klofutar et al., 2010) |
| M _{DG} | 611.73 | Diglyceride molecular mass / kg kmol ⁻¹ | (Klofutar et al., 2010) |
| M _{MG} | 351.91 | Monoglyceride molecular mass / kg kmol ⁻¹ | (Klofutar et al., 2010) |
| M _G | 92.09 | Glycerol molecular mass / kg kmol ⁻¹ | / |
| M _A | 32.05 | Alcohol molecular mass / kg kmol ⁻¹ | / |
| M _{AE} | 291.87 | Alkyl ester molecular mass / kg kmol ⁻¹ | (Klofutar et al., 2010) |
| ρ _{TG} | Variable | Triglyceride density / kg m ⁻³ | (Hilal et al., 2004) |
| ρ _{DG} | Variable | Diglyceride density / kg m ⁻³ | (Hilal et al., 2004) |
| ρ _{MG} | Variable | Monoglyceride density / kg m ⁻³ | (Hilal et al., 2004) |
| ρ _G | Variable | Glycerol density / kg m ⁻³ | (Hilal et al., 2004) |
| ρ _A | Variable | Alcohol density / kg m ⁻³ | (Hilal et al., 2004) |
| ρ _{AE} | Variable | Alkyl ester density / kg m ⁻³ | (Hilal et al., 2004) |
| k _c | k _{c0} exp(-E _a /(RT)) d _{ref} /d | Mass transfer coefficient / m s ⁻¹ | (Klofutar et al., 2010) |
| a | 6φ/d | Specific surface area / m ⁻¹ | / |
| k ₁ | A ₁ exp(-E _{a1} /(RT)) | Triglyceride transesterification forward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| k ₂ | A ₂ exp(-E _{a2} /(RT)) | Diglyceride transesterification forward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| k ₃ | A ₃ exp(-E _{a3} /(RT)) | Monoglyceride transesterification forward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| k ₄ | A ₄ exp(-E _{a4} /(RT)) | Triglyceride transesterification backward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| k ₅ | A ₅ exp(-E _{a5} /(RT)) | Diglyceride transesterification backward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| k ₆ | A ₆ exp(-E _{a6} /(RT)) | Monoglyceride transesterification backward reaction rate constant / m ³ kmol ⁻¹ s ⁻¹ | (Klofutar et al., 2010) |
| T | Variable | Time / s | / |

Table 3. Descriptions and numerical values of the symbols in Equations (1)–(7)

Experiments were also performed by Ataya et al. (2007) at ambient temperature to investigate the effects of mass transfer during the transesterification reaction of canola oil with methanol (CH_3OH) to form fatty acid methyl esters using a sulfuric acid (H_2SO_4) catalyst at a $\text{CH}_3\text{OH}/\text{oil}$ molar ratio of 6:1. Experiments at ambient conditions result in reaction rates that are slow enough to permit the effects of mass transfer on the transesterification reaction to become more evident than at higher temperatures. The influence of mass transfer was investigated by comparing a mixed versus quiescent two-phase reaction and changing a two-phase reaction to a single-phase reaction through the addition of a solvent, tetrahydrofuran (Ataya et al., 2007). The presence of tetrahydrofuran minimizes the mass transfer problem normally encountered in heterogeneous systems (Soriano et al., 2009). Vegetable oil such as corn, sunflower, rapeseed, soybean, and palm oil may also be completely transesterified into biodiesel fuel in short time because of high mass transfer rate in the homogeneous solution formed by adding environment-friendly solvent of dimethyl ether (Guan et al., 2007). The feasibility of fatty acid methyl ester as a co-solvent used to increase the mass transfer between oil and methanol was investigated by Park et al. (2009).

The solution to the new system model acknowledging mass transfer and kinetics is presented in Fig. 2–6. The whole $[\text{TG}]$, $[\text{DG}]$, $[\text{MG}]$, $[\text{G}]$, $[\text{A}]$ and $[\text{AE}]$ versus t set of solutions for arbitrary conditions and initial $[\text{TG}]_0$, $[\text{DG}]_0$, $[\text{MG}]_0$, $[\text{G}]_0$, $[\text{A}]_0$ and $[\text{AE}]_0$ were obtained using the fourth-order Runge–Kutta method in the form described by Klofutar et al. (2010). The value of each parameter of Equations (2)–(7) is given in Table 3. The symbols which are not explained in Table 3 are gas constant (R), temperature (T), distribution coefficient of triglyceride in continuous and dispersed phase (D) (Hilal et al., 2004), pre-exponential factors (A_i) (Klofutar et al., 2010), activation energies (E_{ai}) (Klofutar et al., 2010), dispersed phase drop size (d) (Klofutar et al., 2010), reference dispersed phase drop size (d_{ref}) (Klofutar et al., 2010), and dispersed phase volume fraction (ϕ) (Klofutar et al., 2010).



$$\frac{d[\text{TG}]}{dt} = k_c a ([\text{TG}]_i - [\text{TG}]) - k_1 [\text{TG}][\text{A}] + k_4 [\text{DG}][\text{AE}] \quad (2)$$

$$\frac{d[\text{DG}]}{dt} = k_1 [\text{TG}][\text{A}] - k_2 [\text{DG}][\text{A}] - k_4 [\text{DG}][\text{AE}] + k_5 [\text{MG}][\text{AE}] \quad (3)$$

$$\frac{d[\text{MG}]}{dt} = k_2 [\text{DG}][\text{A}] - k_3 [\text{MG}][\text{A}] - k_5 [\text{MG}][\text{AE}] + k_6 [\text{G}][\text{AE}] \quad (4)$$

$$\frac{d[G]}{dt} = k_3[MG][A] - k_6[G][AE] \quad (5)$$

$$\frac{d[A]}{dt} = -k_1[TG][A] - k_2[DG][A] - k_3[MG][A] + k_4[DG][AE] + k_5[MG][AE] + k_6[G][AE] \quad (6)$$

$$\frac{d[AE]}{dt} = k_1[TG][A] + k_2[DG][A] + k_3[MG][A] - k_4[DG][AE] - k_5[MG][AE] - k_6[G][AE] \quad (7)$$

The examination of Fig. 2 reveals the sigmoid curve for the production of methyl esters and glycerol. This indicates the low reaction rate or the delay at the beginning which is followed by a sudden surge and finally a lower rate as the reactions approach equilibrium. This is the typical behaviour for autocatalytic reactions or reactions with changing mechanisms. Since the transesterification reaction of triglycerides is not known to be an autocatalytic reaction, a second possibility is hypothesized as a mass transfer-controlled region (low rate) followed by a kinetics-controlled region (high rate) and a final low-rate region as the equilibrium is approached. This hypothesis was in more detail discussed in the previous paragraphs and will be supported with the simulated data in the following figures.

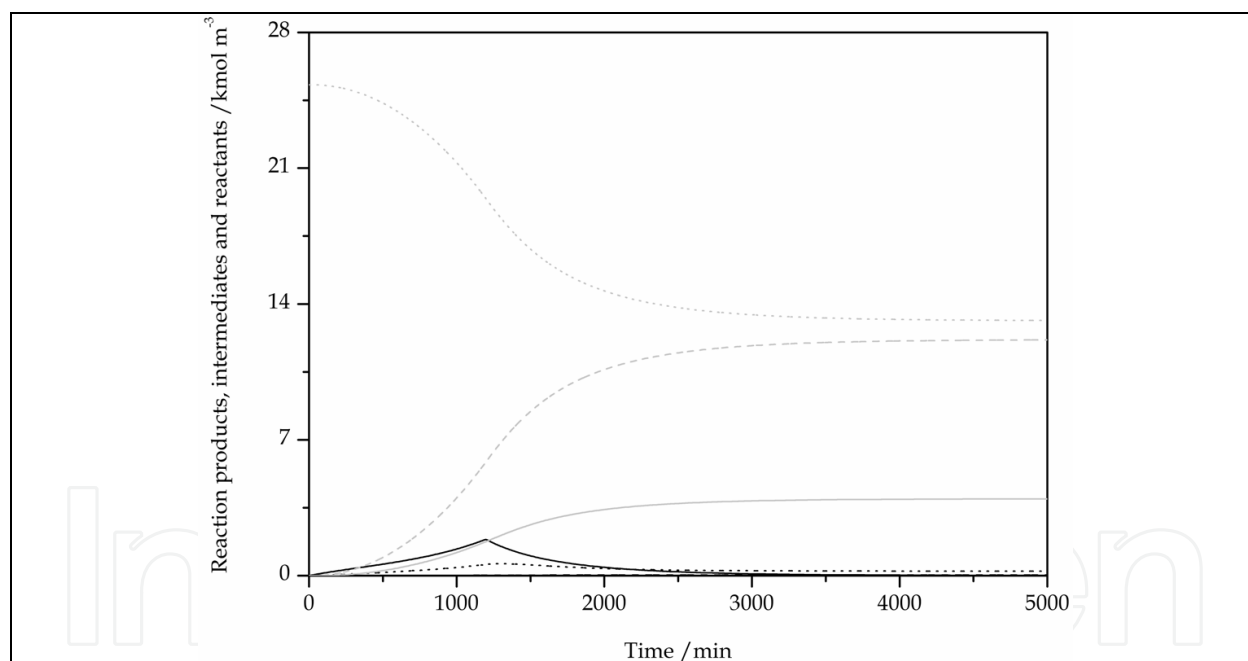


Fig. 2. The composition of the reaction mixture in dispersed phase during the transesterification of sunflower oil with catalyst concentration of 1 wt. % at 0 °C and Reynolds number (Re) of 49.2 (impeller speed of 100 rpm); (—) triglycerides; (.....) diglycerides; (---) monoglycerides; (—) glycerol; (.....) alcohol; (---) alkyl esters; the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

Consequently, the effect of mixing was studied. In this transesterification reaction, the reactants initially form a two-phase liquid system. The rate is diffusion-controlled and the poor diffusion between the phases results in a low rate. As methyl esters are formed, they act as the mutual solvent for reactants, intermediates and products and a single-phase system is

formed. This was substantiated with simulations by differing impeller speeds showing that the low-rate region is practically absent when using 200 rpm ($Re = 98.4$) or more (Fig. 3).

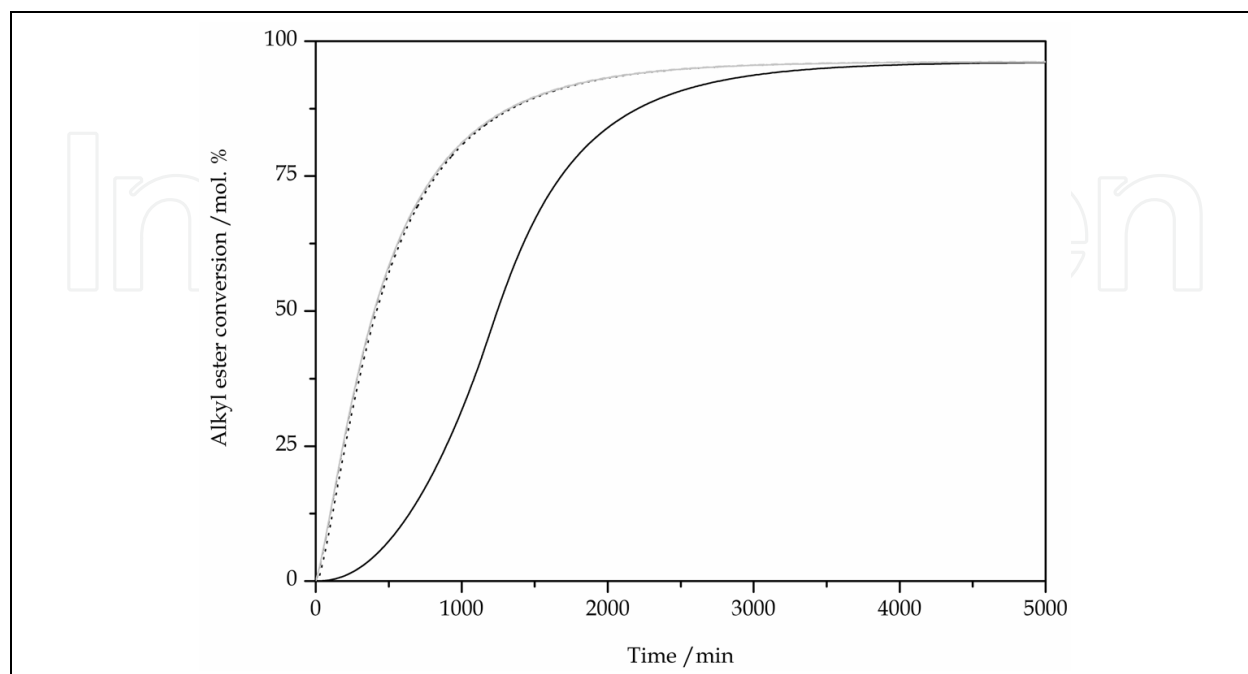


Fig. 3. The effect of mixing intensity and time on the overall conversion of sunflower oil with catalyst concentration of 1 wt. % to alkyl esters at 0 °C; (—) $Re = 49.2$ ($N = 100$ rpm); (.....) $Re = 98.4$ ($N = 200$ rpm); (---) $Re = 147.6$ ($N = 300$ rpm); (—) $Re = 196.8$ ($N = 400$ rpm); (.....) $Re = 246.0$ ($N = 500$ rpm); (---) $Re = 295.2$ ($N = 600$ rpm); (—) $Re = 344.4$ ($N = 700$ rpm); (.....) $Re = 393.6$ ($N = 800$ rpm); (---) $Re = 442.8$ ($N = 900$ rpm); the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

Results revealed that during the very early stages of the reaction, the mixture is separated into two phases. However, as the process was continued, a single phase was observed at the time corresponding either to inflection point or maximum in the concentration–time diagram. Fig. 3 summarizes this delay or the low-rate region as a function of the mixing intensity at a constant reaction temperature of 0 °C. As expected, this time lag decreased as the mixing intensity was increased and reached a practically constant value of less than 1 min for Re greater than 98.4.

Subsequently, the effect of temperature was studied. The temperature dependency of the overall alkyl ester formation reaction rate is presented in Fig. 4 and 5 at two different mixing intensities. This dependency is similar to the effect of the mixing intensity and has to be analyzed separately for the previously hypothesized mass transfer- and kinetics-controlled regions. The time of the mass transfer-controlled region is shortened as temperature is increased (Fig. 4 and 5) which is due to the higher energy level of molecules resulting in more fruitful diffusion into continuous phase. The improved solubility of triglycerides in alcohol at elevated temperatures is also partially responsible for this behaviour. Mass transfer-controlled region is reduced from 1200 min to about 180 min as temperature is increased from 0 °C to 10 °C at $Re = 98.4$ (Fig. 4). At higher mixing intensities, mass transfer-controlled region is short and this effect is not significant (Fig. 5).

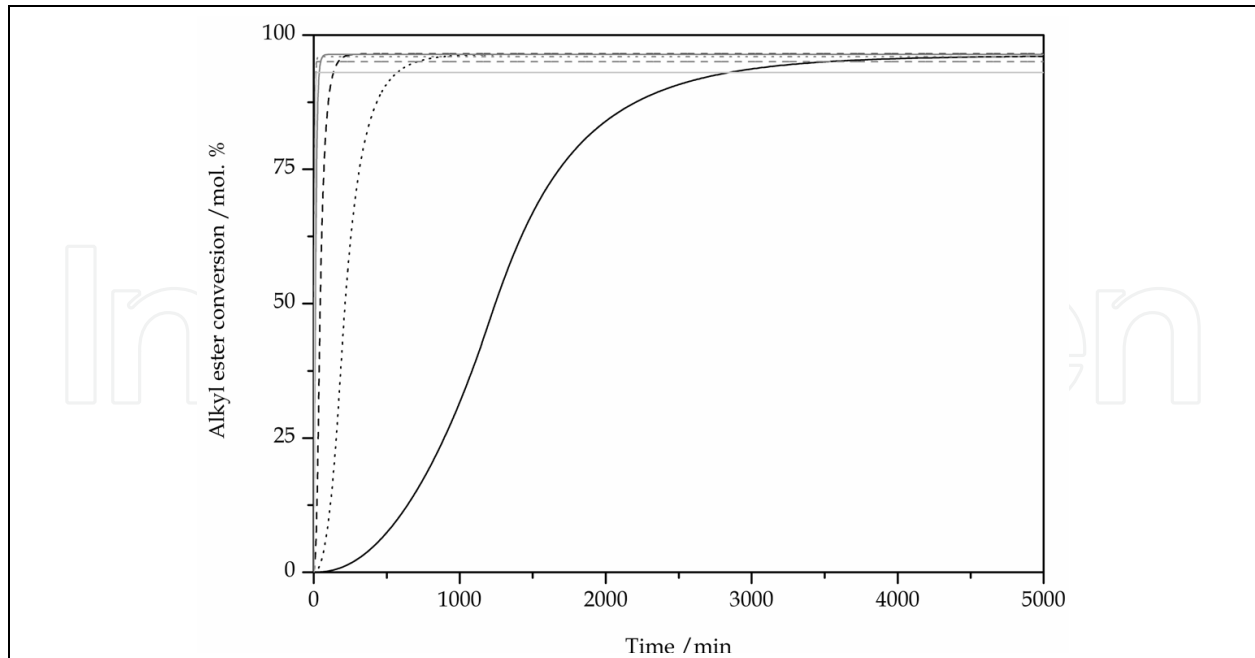


Fig. 4. The effect of temperature and time on the overall conversion of sunflower oil with catalyst concentration of 1 wt. % to alkyl esters at $Re = 49.2$ ($N = 100$ rpm); (—) 0 °C; (.....) 10 °C; (---) 20 °C; (-·-·) 30 °C; (.....) 40 °C; (---) 50 °C; (—) 60 °C; the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

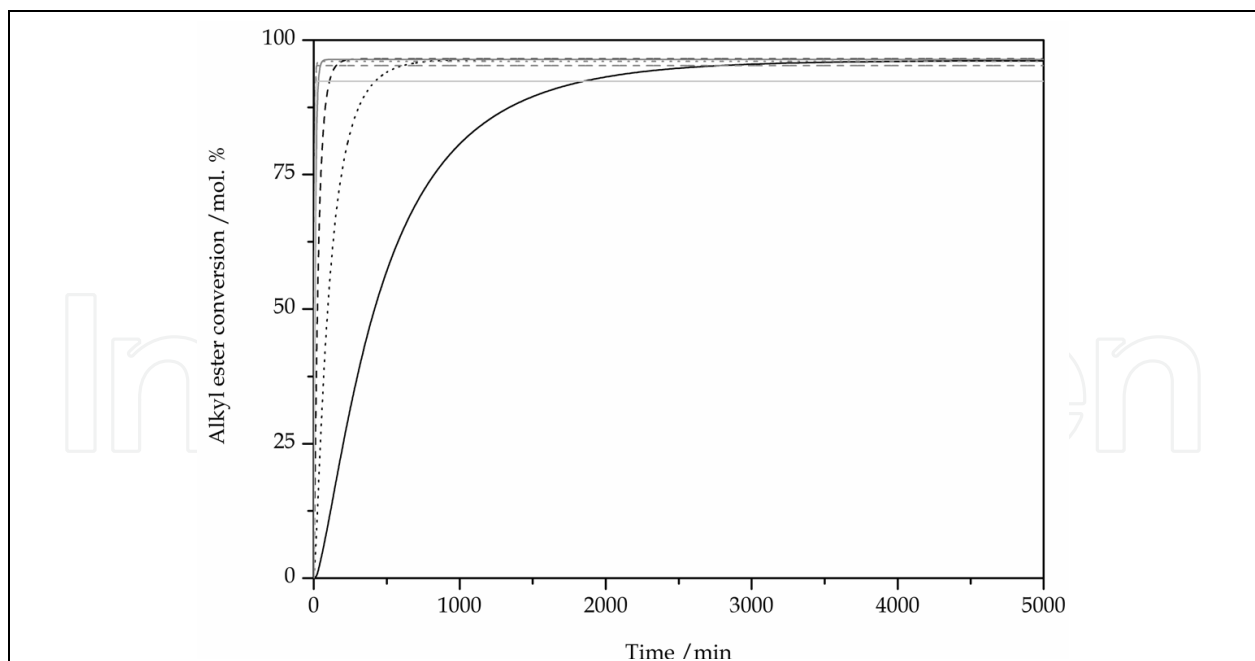


Fig. 5. The effect of temperature and time on the overall conversion of sunflower oil with catalyst concentration of 1 wt. % to alkyl esters at $Re = 98.4$ ($N = 200$ rpm); (—) 0 °C; (.....) 10 °C; (---) 20 °C; (-·-·) 30 °C; (.....) 40 °C; (---) 50 °C; (—) 60 °C; the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

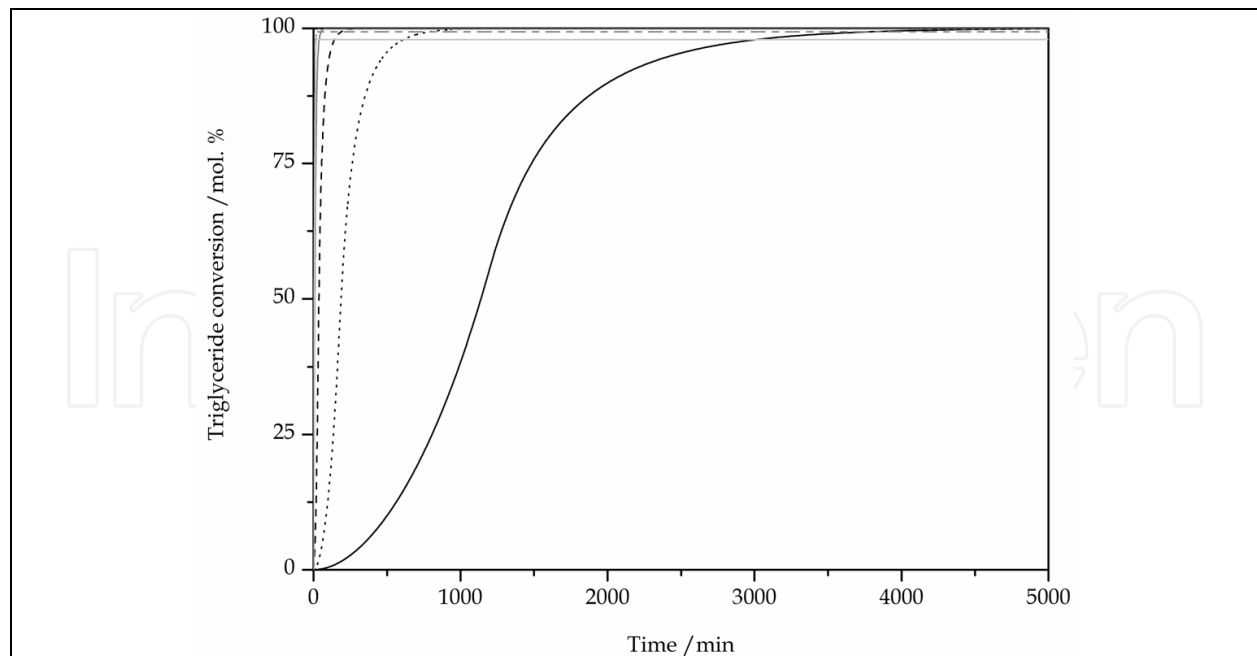


Fig. 6. The effect of temperature on the triglycerides conversion in sunflower oil with catalyst concentration of 1 wt. % at $Re = 49.2$ ($N = 100$ rpm); (—) 0 °C; (.....) 10 °C; (---) 20 °C; (—) 30 °C; (- · - · -) 40 °C; (- - -) 50 °C; (—) 60 °C; the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

The effects of impeller speed and temperature are thus predominant in influencing the mass-transfer-determined rate of the biodiesel production process in batch reactors. Twenty-one simulations of reactions were carried out all in all varying temperature and impeller speed using 1 wt. % of potassium hydroxide concentration in sunflower oil. Fig. 6 represents the triglyceride conversion change with time for the reactions using 100 rpm at 0 °C, 10 °C, 20 °C, 30 °C, 40 °C, 50 °C and 60 °C. In all cases, triglyceride conversions were very low during the beginning of reactions, which involved a low methyl ester production rate at this stage. The conversions then increased and at the end remained approximately constant as equilibrium was approached. Nouredini & Zhu (1997) also observed these three regions of different rate behaviour. As mentioned, this behaviour is typical for the processes with changing mechanisms. The observed low-rate region was again due to the immiscibility of sunflower oil and methanol during the first stages of the reactions. As mentioned, in this region, the rate is controlled by mass transfer.

2.2 Semi-batch reactors

In a semi-batch reactor, the immiscibility of oil in alcohol (canola oil and methanol were studied) provides a mass transfer challenge in the early stages of the transesterification of oil (specifically, canola oil) in the production of fatty acid methyl esters (biodiesel) (Dube et al., 2007).

2.3 Continuous reactors

Continuous reactor technologies enhance reaction rate, reduce molar ratio of alcohol to oil and energy input by intensification of mass transfer and heat transfer and in situ product separation, thus achieving continuous product in a scalable unit (Qui et al., 2010).

One of the possible continuous reactors for biodiesel production process is an oscillatory flow reactor. An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficient heat and mass transfer, whilst maintaining plug flow (Harvey et al., 2003).

Another possibility is a continuous tubular reactor, in which at low conversion values (< 25–35%), the system has mass transfer limitations due to the immiscibility of the oil–methanol system (Busto et al., 2006).

Yet another possibility is a packed bed reactor, in which kinetics and mass transfer of free fatty acids esterification with methanol are a key pre-treatment in biodiesel production. The collected experimental data may be interpreted by means of a mono-dimensional packed bed reactor model in which the external mass transfer limitation (fluid-to-particle) is accounted for (Santacesaria et al., 2007a). Experiments were performed by Ataya et al. (2008a) to study the mass-transfer limitations during the acid-catalyzed transesterification reaction of triglyceride with methanol (CH_3OH) to fatty acid methyl ester (biodiesel). The rate constant at two-phase conditions (largest velocity, smallest packing particle size, and maximum pressure gradient) are comparable to that obtained at single-phase conditions, indicating that the mass-transfer limitations for two-phase experiments can be effectively overcome using a liquid-liquid packed bed reactor. The diminished mass transfer is explained by the formation of a new interfacial area between the two liquid phases, caused by the droplets being momentarily deformed into an elongated non-spherical shape as they pass through the openings between the solid particles of the packed bed (Ataya et al., 2008a).

The fourth possibilities are a slurry reactor and a loop reactor. Both the well-stirred slurry reactor and spray tower loop reactor show liquid–solid phase mass transfer limitations (Santacesaria et al., 2007b). Different configurations and dynamics of single air/alcohol gas-liquid compound drops in vegetable oil may largely improve mass transfer in a slurry reactor (Duangsuwan et al., 2009). The kinetic model that is developed on the basis of several batch runs is also able to simulate the behaviour of dynamic tubular loop reactor, providing that the external mass transfer resistance is properly accounted for. The mass transfer coefficient is satisfactorily modelled using correlations available in literature (Tesser et al., 2009).

The fifth possibility is a continuous reactor with static mixing. A novel continuous static reactor concept improves mass transfer in two-phase chemical reactions between one and two orders of magnitude (Massingill et al., 2008).

The sixth possibility is a film reactor. This reactor is a co-current, constant diameter (0.01 m), custom-made packed column where the mass transfer area between the partially miscible methanol-rich and vegetable oil-rich phases is created in a non-dispersive way, without the intervention of mechanical stirrers or ultrasound devices (Narvaez et al., 2009).

The seventh possibility is a continuous reactor with counter flow. In the latter, the excess methanol is subjected to a mass transfer from the liquid phase into the gas phase, which is withdrawn through the head of the reactor and condensed in an external condenser unit (Iglauer & Warnecke, 2009).

The eighth possibility is a micro-structured reactor. Micro-structured reactors have an equivalent hydraulic diameter up to a few hundreds of micrometers and, therefore, provide high mass and heat transfer efficiency increasing the reactor performance drastically, compared to the conventional one. Particular attention is given to the identification of the parameters that control the flow pattern formed in micro-capillaries regarding the mass

transfer efficiency (Kashid & Kiwi-Minsker, 2009). The homogeneous state in the micro-tube should be a benefit for the transesterification of waste cooking oil due to the enhancement of the mass transfer between oil and methanol (Guan et al., 2010).

The ninth possibility is a membrane reactor. A new alternative technology, using hydrophobic porous membranes, can be used to prevent bulk mixing of the two phases and facilitate contact and mass transfer of species between the two phases (Sdrula, 2010).

2.4 Bioreactors

One of the possible organisms used for biodiesel production process are fungi. The initial reaction rate is increased notably (204%) with oil pre-treatment on the cells before catalyzing the reaction, which is possibly due to the improved mass transferring of substrates (Zeng et al., 2006). The accumulated glycerol influences whole cell stability through mass transfer limitation only, while the accumulated methyl ester influences whole cell stability through both mass transfer limitation and product inhibition (Li et al., 2008). Halim et al. (2009) studied continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor; investigating optimization using response surface methodology and mass transfer, specifically the effect of mass transfer in the packed bed bioreactor has been studied extensively. Models for fatty acid methyl ester yield are developed for cases of reaction control and mass transfer control. The results show very good agreement compatibility between mass transfer model and the experimental results obtained from immobilized lipase packed bed reactor operation, showing that in this case the fatty acid methyl ester yield is mass transfer-controlled (Halim et al., 2009). A kinetic model was developed by Al-Zuhair et al. (2009) to describe a bioreactor system, taking into consideration the mass transfer resistances of the reactants. The experimental results were used to determine the kinetic parameters of the proposed model and to determine the effect of mass transfer (Al-Zuhair et al., 2009).

Sim et al. (2009) studied the effect of mass transfer and enzyme loading on the biodiesel yield and reaction rate in the enzymatic transesterification of crude palm oil. Efforts in minimizing mass transfer effects in enzymatic transesterification of crude palm oil in a biphasic system have always been the compromise between enzyme loading and agitation speed, therefore, effect of enzyme loading and agitation speed on fatty acid methyl ester productivity in terms of intrinsic and external mass transfer limitations and the effective reaction time may be determined using factorial design. Graphical plots of experimental results reveal that the mass transfer effect for the transport of reactant from bulk liquid to immobilized lipase and within the intra-particle of immobilized lipase are absent at 150 rpm and 6.65% enzyme loading (Sim et al., 2009). In the case of continuous process, circulation and long-term continuous system are investigated for development of efficient mass transfer system (Lee et al., 2010). The aim of the study by Sotoft et al. (2010) was to determine reaction enthalpy for the enzymatic transesterification and to elucidate the mass transfer and energetic processes taking place. Although it is possible to determine thermodynamic properties such as reaction enthalpy and reaction rate, the difficulty in actually measuring the true non-mass transfer-limited reaction kinetics is exposed by the high time resolution of isothermal calorimetry (Sotoft et al., 2010).

Another possibility are bacteria, for which employment of immobilization seems to result in a decrease in the maximum rate (v_{\max}) and an increase in the Michaelis constant (K_M), most likely due to the mass transfer resistance arising from formation of micelles during the lipase immobilization process (Liu & Chang, 2008).

Yet another possibility are algae, for which maximizing cost efficient mass transfer of CO₂ to cells in an aqueous environment is not a trivial task for large-scale liquid culture systems as is anticipated for outdoor algal cultures (Xu et al., 2009).

However, in all these organisms the reaction catalysts are the enzymes themselves, critical aspects of these being mass transfer limitations, use of solvents and water activity together with process considerations and evaluation of possible reactor configurations, if industrial production with enzymes is to be carried out (Ejerbaek et al., 2009). However, these heterogeneous acid- and enzyme-catalyzed systems still suffer from serious mass transfer limitation problems and therefore are not favourable for industrial application. Nevertheless, a few latest technological developments that have the potential to overcome the mass transfer limitation problem such as oscillatory flow reactor, ultrasonication, microwave reactor and co-solvent use are being studied (Lam et al., 2010).

2.5 Downstream processing

To remove the unwanted side products (e.g. glycerol) from the wanted main product (biodiesel), adsorption may be used. Industrial adsorption units with beads (3.18 mm silica beads were studied) suffer from mass transfer limitations inside the pellet pores, and for the particle size investigated by Yori et al. (2007), the breakthrough point (output concentration per input concentration of 1%, $C/C_0 = 0.01$) was located at about one-half of the time of full saturation. Assuming a linear isotherm gives erroneous results; fitting the experimental breakthrough curves produces underestimated values of the Henry's adsorption constant and of the mass transfer resistances. Accordingly, breakthrough curves are fairly well predicted using an irreversible isotherm, a shrinking-core adsorption model, and common correlations for the mass transfer coefficients (Yori et al., 2007). To remove the unwanted glycerol from the wanted biodiesel, glycerol may also be used as a substrate in an enzyme reaction. Volpato et al. (2009) studied the effects of oxygen volumetric mass transfer coefficient and pH on lipase production by *Staphylococcus warneri* EX17. The principal objectives of this study were to evaluate the kinetics of lipase production by *Staphylococcus warneri* EX17 under different oxygen volumetric mass transfer coefficients ($k_{L,a}$) and pH conditions in submerged bioreactors, using glycerol (a biodiesel by-product) as a carbon source (Volpato et al., 2009). To remove the unwanted glycerol from the wanted biodiesel, glycerol may also be used as a reactant in a chemical reaction for the production of dichloropropanol. The reaction is conducted at high agitation speed in order to avoid mass transfer limitation between glycerol and hydrochloric acid gas (Song et al., 2009).

To remove the unwanted side products (e.g. salts) from the dispersed phase after removing glycerol (mostly water), desalination may be used. A competent grasp of thermodynamics and heat and mass transfer theory, as well as a proper understanding of current desalination processes, is essential for ensuring beneficial improvements in desalination processes (Semiati, 2008). To remove the unwanted salts from the dispersed phase, adsorption may also be used. Kinetic experiments show that the rate of mass transfer in the adsorbent/liquid binary system is high (Carmona et al., 2009).

Mass transfer also plays an important role during biodiesel's final application as a fuel, usually for an engine. For example, engine internal processes are usually studied by means of exergy balances based on engine indicating data, which provides information about the impact of biodiesel blending on the amount of fuel exergy exchanged through heat, work and mass transfer (Bueno et al., 2009). Also, the improved physical (mass transfer, filtering of C-containing species) and chemical (reaction kinetics) processes during hydrocarbon-selective catalytic reduction over powders compared to monoliths leads to better initial

catalyst activity, but it also accelerates catalyst deactivation which lead to increased diffusion limitations (Sitshebo et al., 2009).

3. Kinetics-determined rate of biodiesel production process

3.1 Influence of lipid and alcohol on reaction rate

The transesterification of oils (triglycerides) with simple alcohols in the presence of a catalyst has long been the preferred method for preparing biodiesel. As already mentioned the initial mass transfer-controlled region is not significant using the impeller speed of 600 rpm, high temperature, or the molar ratio of alcohol to oil higher than 6:1.

The general, overall apparent reaction of the transesterification of triglycerides with alcohol is reversible and every triglyceride molecule can react with three molar equivalents of alcohol (usually methanol) to produce glycerol and three fatty acid alkyl ester molecules. Fatty acid originating chains vary in composition depending on the source of triglycerides. The reaction of transesterification is highly dependent on oil quality, especially in terms of free fatty acid and water content. Today, most of biodiesel comes from the transesterification of edible resources, such as animal fats, vegetable oils, and even waste cooking oils, in the conditions of alkaline and acid catalysis. Conventional oils, such as canola oil, sunflower oil, and soybean oil, are usually employed for the biodiesel synthesis under acidic conditions (Santacesaria et al., 2007b). In novel process studies, the use of tin chloride, lipases, and supercritical alcohol without catalyst is being investigated, using conventional oils, such as canola oil, sunflower oil, soybean oil, and palm oil. In most industrial biodiesel processes, in which biodiesel is synthesized under alkaline conditions, oils such as canola oil, sunflower oil, soybean oil, palm oil, olive oil, *Brassica carinata* oil, and *Pongamia pinnata* oil were used (Nouredini & Zhu, 1997; Vicente et al., 2006; Bambase et al., 2007; Stamenkovic et al., 2008) Canola oil is the preferred oil feedstock for the biodiesel production in most of Europe,

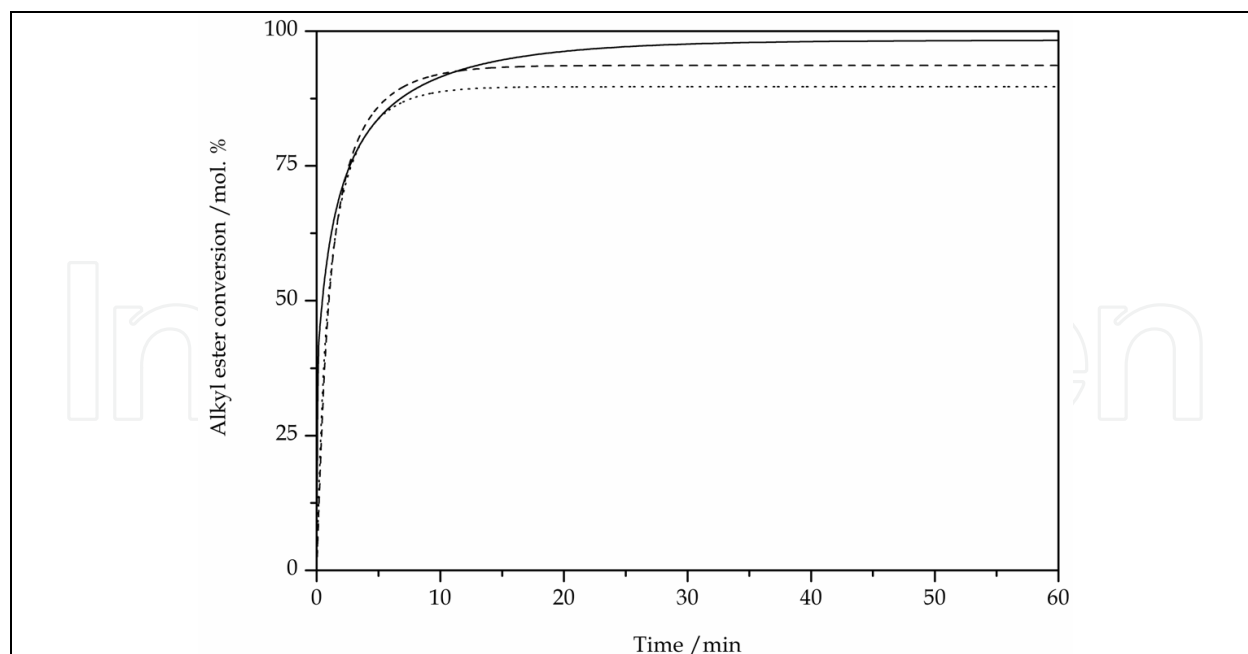


Fig. 7. The effect of lipid on the alkyl ester conversion in oil with catalyst concentration of 1 wt. % at $Re \rightarrow \infty$ and 65°C ; (—) *Brassica carinata* oil; (.....) sunflower oil; (---) canola oil; the parameters for simulation were obtained from the literature (Vicente et al., 2006, Klofutar et al., 2010)

| Reaction temperature /°C | N / min ⁻¹ | k ₁ / m ³ kmol ⁻¹ min ⁻¹ | k ₂ / 10 ¹ m ³ kmol ⁻¹ min ⁻¹ | k ₃ / 10 ⁻¹ m ³ kmol ⁻¹ min ⁻¹ | k ₄ / 10 ¹ m ³ kmol ⁻¹ min ⁻¹ | k ₅ / 10 ¹ m ³ kmol ⁻¹ min ⁻¹ | k ₆ / 10 ⁻² m ³ kmol ⁻¹ min ⁻¹ | Oil | C _c / wt. % | Literature |
|--------------------------|-----------------------|--|--|---|--|--|---|--------------------|------------------------|-------------------------|
| 25 | 600 | 0.07 | 0.02 | 2.20 | 0.03 | 0.01 | 1.60 | Sunflower | 0.50 | (Vicente et al., 2005) |
| 35 | 600 | 0.20 | 0.17 | 2.70 | 0.10 | 0.22 | 1.10 | Sunflower | 0.50 | |
| 45 | 600 | 0.37 | 0.38 | 3.20 | 0.19 | 0.44 | 0.77 | Sunflower | 0.50 | |
| 55 | 600 | 0.80 | 1.05 | 3.40 | 0.60 | 1.59 | 0.35 | Sunflower | 0.50 | |
| 65 | 600 | 1.50 | 2.30 | 4.00 | 1.37 | 4.14 | 0.26 | Sunflower | 0.50 | |
| 25 | 600 | 0.11 | 0.03 | 2.60 | 0.04 | 0.02 | 1.30 | Sunflower | 1.00 | |
| 35 | 600 | 0.30 | 0.25 | 3.70 | 0.15 | 0.31 | 0.77 | Sunflower | 1.00 | |
| 45 | 600 | 0.50 | 0.70 | 4.50 | 0.31 | 1.00 | 0.30 | Sunflower | 1.00 | |
| 55 | 600 | 1.55 | 2.05 | 6.10 | 0.85 | 2.25 | 0.12 | Sunflower | 1.00 | |
| 65 | 600 | 3.06 | 3.25 | 5.40 | 2.39 | 5.75 | 0.09 | Sunflower | 1.00 | |
| 25 | 600 | 0.15 | 0.04 | 4.90 | 0.07 | 0.04 | 0.40 | Sunflower | 1.50 | |
| 35 | 600 | 0.40 | 0.43 | 6.00 | 0.20 | 0.47 | 0.05 | Sunflower | 1.50 | |
| 45 | 600 | 0.74 | 1.19 | 7.40 | 0.50 | 1.26 | 0.06 | Sunflower | 1.50 | |
| 55 | 600 | 2.05 | 3.01 | 8.30 | 1.09 | 2.95 | 0.01 | Sunflower | 1.50 | |
| 65 | 600 | 4.00 | 5.50 | 9.10 | 2.70 | 6.55 | 0.01 | Sunflower | 1.50 | |
| 25 | 600 | 0.05 | 0.02 | 1.98 | 0.03 | 0.01 | 1.10 | <i>B. carinata</i> | 0.50 | (Vicente et al., 2006) |
| 35 | 600 | 0.22 | 0.16 | 2.52 | 0.11 | 0.23 | 1.00 | <i>B. carinata</i> | 0.50 | |
| 45 | 600 | 0.40 | 0.40 | 2.70 | 0.20 | 0.44 | 0.67 | <i>B. carinata</i> | 0.50 | |
| 55 | 600 | 0.75 | 1.01 | 3.90 | 0.68 | 1.70 | 0.05 | <i>B. carinata</i> | 0.50 | |
| 65 | 600 | 1.30 | 2.20 | 4.08 | 1.45 | 4.24 | 0.26 | <i>B. carinata</i> | 0.50 | |
| 25 | 600 | 0.11 | 0.03 | 3.30 | 0.05 | 0.03 | 1.00 | <i>B. carinata</i> | 1.00 | |
| 35 | 600 | 0.28 | 0.24 | 3.72 | 0.14 | 0.32 | 0.44 | <i>B. carinata</i> | 1.00 | |
| 45 | 600 | 0.55 | 0.69 | 4.20 | 0.30 | 1.01 | 0.30 | <i>B. carinata</i> | 1.00 | |
| 55 | 600 | 1.59 | 2.15 | 6.00 | 0.97 | 2.39 | 0.11 | <i>B. carinata</i> | 1.00 | |
| 65 | 600 | 3.10 | 3.27 | 4.98 | 2.45 | 5.95 | 0.06 | <i>B. carinata</i> | 1.00 | |
| 25 | 600 | 0.20 | 0.06 | 4.68 | 0.06 | 0.08 | 0.50 | <i>B. carinata</i> | 1.50 | |
| 35 | 600 | 0.40 | 0.47 | 6.00 | 0.26 | 0.49 | 0.04 | <i>B. carinata</i> | 1.50 | |
| 45 | 600 | 0.80 | 1.01 | 6.72 | 0.50 | 1.30 | 0.03 | <i>B. carinata</i> | 1.50 | |
| 55 | 600 | 2.90 | 2.95 | 7.98 | 1.12 | 2.89 | 0.02 | <i>B. carinata</i> | 1.50 | |
| 65 | 600 | 4.13 | 5.55 | 9.18 | 2.82 | 6.39 | 0.01 | <i>B. carinata</i> | 1.50 | |
| 40 | 500 | 0.02 | 0.01 | 0.70 | 0.00 | 0.00 | 0.42 | Sunflower | 1.00 | (Klofutar et al., 2010) |
| 50 | 500 | 0.08 | 0.02 | 0.97 | 0.00 | 0.01 | 0.88 | Sunflower | 1.00 | |
| 40 | 500 | 0.04 | 0.02 | 0.65 | 0.01 | 0.03 | 0.47 | Canola | 1.00 | |
| 50 | 500 | 0.09 | 0.05 | 1.56 | 0.01 | 0.07 | 0.61 | Canola | 1.00 | |

Table 4. Reaction rate constants for the triglyceride transesterification reaction with KOH catalyst

partly because canola produces more oil per unit of land area compared to other oil sources. *Brassica carinata*, a native plant of Ethiopia, is a promising alternative oilseed crop for the biodiesel production in the Mediterranean area. It generally has high levels of undesirable glucosinolates and erucic acid which, however; do not affect biodiesel purity, maximum conversion and purification step.

The effect of canola, sunflower, and *Brassica carinata* oil on alkyl (methyl) ester conversion with the catalyst concentration of 1 wt. % at 65 °C is presented in Fig. 7. Under the mentioned conditions, the maximal conversion was achieved with the biodiesel production process using *Brassica carinata* oil.

As already mentioned, the maximum conversion in transesterification equilibrium stage depends on the oil itself, especially in terms of the composition of fatty acids bonded to glycerol. Generally, a vegetable oil with lower iodine value is more suitable for biodiesel production. From this point of view, steric interactions must be considered as an important factor in attempts to achieve the highest equilibrium conversion. In Table 4 and 5 the influence of lipid on the calculated reaction rate constants for the forward and backward reactions is presented.

| Reaction temperature / °C | N / min ⁻¹ | k ₁ / 10 ⁻¹ m ³ kmol ⁻¹ min ⁻¹ | k ₂ / 10 ⁻¹ m ³ kmol ⁻¹ min ⁻¹ | k ₃ / 10 ⁻¹ m ³ kmol ⁻¹ min ⁻¹ | k ₄ / 10 ⁻¹ m ³ kmol ⁻¹ min ⁻¹ | k ₅ / m ³ kmol ⁻¹ min ⁻¹ | k ₆ / 10 ⁻² m ³ kmol ⁻¹ min ⁻¹ | Oil | C _c / wt. % | Literature |
|---------------------------|-----------------------|---|---|---|---|--|---|-----------|------------------------|--------------------------|
| 50 | 300 | 0.50 | 2.15 | 2.42 | 1.10 | 1.23 | 0.70 | Soybean | 0.20 | (Noureddini & Zhu, 1997) |
| 25 | 400 | 0.07 | 0.20 | 1.37 | 0.01 | 0.01 | 0.54 | Sunflower | 0.50 | (Bambase et al., 2007) |
| 40 | 400 | 0.22 | 0.65 | 2.28 | 0.03 | 0.03 | 1.28 | Sunflower | 0.50 | |
| 60 | 400 | 0.50 | 1.00 | 1.03 | 1.35 | 0.41 | 5.99 | Sunflower | 0.25 | |
| 60 | 400 | 0.90 | 3.48 | 4.88 | 0.09 | 0.13 | 3.80 | Sunflower | 0.50 | |
| 60 | 400 | 2.31 | 4.49 | 8.77 | 0.17 | 0.11 | 6.32 | Sunflower | 1.00 | |
| 60 | 600 | 1.32 | 3.23 | 8.61 | 0.20 | 0.25 | 6.06 | Sunflower | 0.50 | |

Table 5. Reaction rate constants for the triglyceride transesterification reaction with NaOH catalyst

3.2 Influence of temperature on reaction rate

When agitation speeds are in the range of 400–600 rpm and mass transfer limitations are practically eliminated, temperature becomes the most influential factor affecting the apparent rate of transesterification as system becomes kinetically controlled (Vicente et al., 2005; Vicente et al., 2006; Bambase et al., 2007; Klofutar et al., 2010). The effect of temperature on the transesterification of canola oil (Klofutar et al., 2010), sunflower oil (Vicente et al., 2005; Bambase et al., 2007; Klofutar et al., 2010), and *Brassica carinata* oil

(Vicente et al., 2006) was also studied and the influence of temperature on the calculated reaction rate constants for forward and backward reactions is presented in Table 4 and 5. It was observed that temperature had a noticeable effect on transesterification reactions.

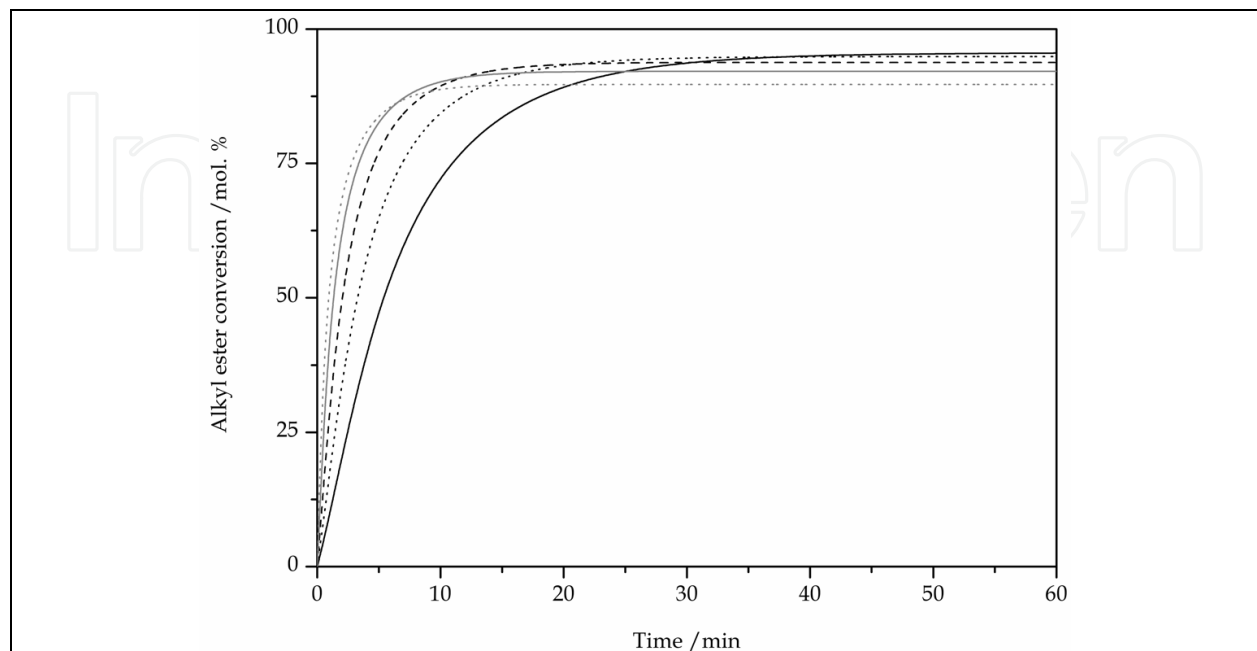


Fig. 8. The effect of temperature on the alkyl ester conversion in sunflower oil with catalyst concentration of 1 wt. % at $Re \rightarrow \infty$; (—) 45 °C; (.....) 50 °C; (---) 55 °C; (—) 60 °C; (· · · · ·) 65 °C; the parameters for simulation were obtained from the literature (Klofutar et al., 2010)

Lower temperature slows down the rate of reactions prolonging the reaction time required to achieve the maximal alkyl ester production. On the other hand, higher reaction temperature results in lower maximal alkyl ester production due to reversible reaction steps (Fig. 8). All reaction rate constants increase with increased temperature, but the backward reaction rate constants increase more intensively in comparison to the forward reaction rate constants. Fig. 8 shows the effect of temperature on the alkyl (methyl) ester conversion in sunflower oil with the catalyst concentration of 1 wt. % (per weight of oil), where KOH was used as the catalyst and the methanol to oil molar ratio of 6:1 was employed at 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C. The apparent rate of esters production increased with the increase in reaction temperature. After 1 h of reaction time or even sooner, the maximal extent of reaction is approached. The temperature of reaction mixture dictates the maximum conversion itself and the rate of transesterification which affects the reaction time required to achieve maximum conversion. From Fig. 8 it follows that after 5 min the conversion of sunflower oil to methyl ester was about 47 mol. %, 65 mol. %, 77 mol. %, 82 mol. %, and 84 mol. % at 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C, respectively. After 60 min the conversion was above 96 mol. %, 95 mol. %, 94 mol. %, 92 mol. %, and 90 mol. % at 45 °C, 50 °C, 55 °C, 60 °C, and 65 °C, respectively.

The obtained reaction rate constants show that the transesterification of sunflower oil is quite sensitive to temperature. The results obtained from examining kinetics suggest that in the temperature range studied, the rates of the forward reactions of transesterification dominate. For the global reaction, $TG + 3 A \rightarrow G + 3 AE$, with 1 wt. % of KOH as the catalyst

(per weight of oil) and the methanol to oil molar ratio of 6:1, the activation energy for the forward reaction is lower than the activation energy of the backward reaction and therefore AE formation is favoured at moderately high temperatures. Overall, the results for sunflower oil suggest that the rates of the forward reactions dominate over the backward ones. A similar trend regarding the activation energies as for the case of the sunflower oil (Klofutar et al., 2010) was obtained for the activation energies of the transesterification of soybean oil by Nouredini & Zhu (1997), who obtained the maximal value of E_a for the reaction of the transesterification of diglycerol.

3.3 Influence of catalyst on reaction rate

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reactions.

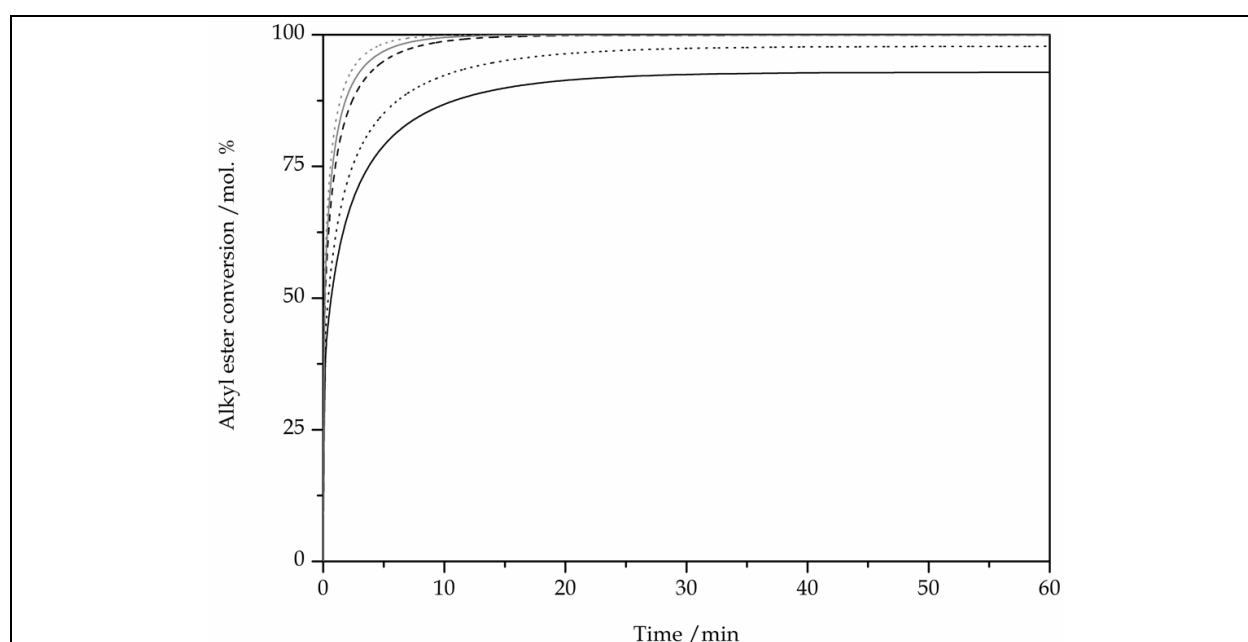


Fig. 9. The effect of catalyst (content) on the alkyl ester conversion in sunflower oil at $Re \rightarrow \infty$ and $65\text{ }^\circ\text{C}$; (—) 0.5 wt. %; (.....) 1.0 wt. %; (---) 1.5 wt. %; (—) 2.0 wt. %; (-·-·-) 2.5 wt. %; the parameters for simulation were obtained from the literature (Vicente et al., 2005)

A common catalyst for transesterification reactions is potassium hydroxide. An advantage of this catalyst is that at the end of reactions the mixture can be neutralized with phosphoric acid, whereas the products of neutralization reaction can be used as an artificial fertilizer.

The common acid-catalyzed processes of the biodiesel production from low-cost raw materials involve the use of mineral acids; this is due to the large amounts of the edible resources with free fatty acids, which are not compatible with the use of base-catalyzed methods. The acid-catalyzed processes and the corresponding kinetic studies included the use of sulphuric acid as the catalyst (Santacesaria et al., 2007b), whereas in another study of Santacesaria et al. (2007a), a sulphonic active group-functionalized copolymer matrix gel was applied as a catalyst as well.

It must be pointed out, however; that major drawbacks – such as reactor corrosion and the substantial generation of by-products and waste materials, including the salts formed as a result of mineral acid neutralization, which must be disposed of in the environment – represent insurmountable problems for the mineral-acid-catalyzed process.

The kinetics of biodiesel production can usually be differentiated by the mechanism of transesterification process. As mentioned before, in the novel kinetic studies of biodiesel production process, the use of tin chloride as a catalyst, lipases as biocatalysts, and supercritical alcohol without catalyst is being investigated.

In most industrial biodiesel processes, however; the oil as a reactant is added to methoxide (methanol and an alkali metal base) and mixed for some time at a temperature just below the boiling point of methanol, followed by settling and washing. This type of process represents the most investigated area of research in the field of base-catalyzed biodiesel production kinetics (Noureddini & Zhu, 1997; Vicente et al., 2006; Bambase et al., 2007; Stamenkovic et al., 2008; Slinn & Kendall, 2009). These base-catalyzed processes and the corresponding kinetic studies include the use of either sodium (Noureddini & Zhu, 1997; Bambase et al., 2007; Slinn & Kendall, 2009) or potassium (Vicente et al., 2006; Stamenkovic et al., 2008, Klofutar et al., 2010) hydroxide as the catalyst.

Fig. 9 shows the effect of catalyst loading on the process of the methanolysis reactions in the catalyst concentration range 0.5–2.5 wt. % at 65 °C. As expected, the alkyl ester production rate increases with catalyst concentration. A lower rate of transesterification is observed at a lower concentration of catalyst (0.5 wt. %) with the swift reaction termination at 89% equilibrium conversion. It is believed that, at this point, all of the available hydroxide catalyst had been saponified. Bambase et al. (2007) observed the same effect of catalyst concentration on reaction system. Increasing the catalyst concentration to 1.5 wt. %, 2.0 wt. % or even 2.5 wt. % speeds up the reactions, giving a more rapid apparent rate of alkyl ester production during the initial period of process although the conversion maximum does not differ much once a critical catalyst content is reached. It does not seem necessary to use the catalyst concentration higher than 1.5 wt. %, since adding surplus hydroxide catalyst leads to the formation of excess soaps resulting in the very low recovery of alkyl (usually methyl) esters during phase separation. At the end, the optimal catalyst loading is highly dependent on the quality of oil, especially in terms of free fatty acid and water content.

4. Conclusion

Fatty acid alkyl (usually methyl) esters, known as biodiesel, have a great potential as the substitutes for conventional diesel fuel. Rudolph Diesel is said to have already conducted experiments with vegetable oils as fuel for his engine in the late 1890s. In recent years, the biodiesel production from vegetable oils and animal fats has gained much attention, because of its eco-friendly nature, liquid state, and easy portability. However, this green fuel production is problematic because it comes into direct competition with the production of food, consequently causing the prices of the latter to increase. We should thus be careful not to extend the production of biofuel so much that it would significantly contribute to the loss of cultivated land. Biodiesel is also more expensive than fossil fuels, which limits its applications. Biofuels appear to be the only realistic short term source of renewable energy as an alternative to the fossil fuels in transportation sector. Their liquid nature and compatibility with traditional fuels are their main strengths. The Renewable Energy Directive (RED) of the European Union requires biofuels (biodiesel and bioethanol) to reach 10% of total automotive fuel consumption by the year 2020. Biofuels should contribute to a 35% CO₂ reduction at the introduction of the new directive, aiming to reach 50% by 2017 (60% for new production plants). On the other hand, diesel continues its strong growth,

while gasoline is in decline. At the same time, the production of biodiesel is growing and it is expected to reach around 18 million tons of biodiesel per year in EU-27 by 2020. This forecast represents around 50% compliance with the EU directive target. The recent suggestion for an EU target of 10% by 2020 is considered ambitious by most analysts. The wide-spread popularity of biodiesel in recent years has also led to the founding of biodiesel-powered electrical plant in Slovenia in August 2010.

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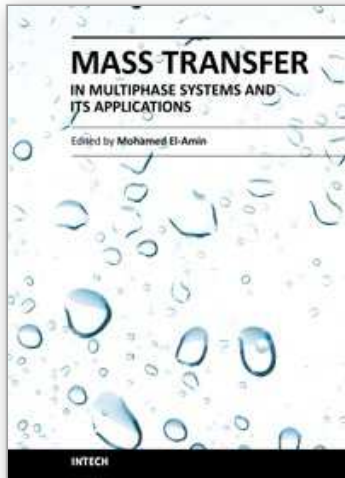
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