Research note

Kinetic Modeling of Sunflower Oil Methanolysis Considering Effects of Interfacial Area of Reaction System

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Abstract
In this study, a kinetic model is proposed for Sunflower oil methanolysis in which the effect of the interfacial area on the reaction system has been investigated. The model is based on the combination of mass transfer and kinetics. Rate constant of the reaction is obtained by fitting of the experimental data with the model. Based on this model, activation energy is equal to E/R=3390 K. This model was applied to the transesterification of soybean oil with some modifications on Misek's equation and interfacial tension correlation. Methyl ester production at two different mixing intensities was evaluated. By using this model, theoretical conversion is calculated and is compared with the experimental data taken from literature. An acceptable agreement has been obtained between two sets of data. Based on the experimental data shown in the paper, agitator speed has no significant effect on the conversion. Therefore, it can be concluded that at a temperature of 55°C or higher, the model parameter approaches to the rate constant of reaction and the agitation speed does not affect the kinetics.

Keywords: *Sunflower Oil, Methanolysis, Kinetic Model, Interfacial Effects*

1. Introduction
With today's increasing concern for the environment and the depletion of fossil-fuel resources, comes a greater awareness for the substitute of petroleum-based fuels to the alternative renewable fuels, especially biodiesel (Ruppel et al., 2008). Most of the biodiesel production is from the alcoholysis (transesterification) process.

Biodiesel is made from heating and mixing of three moles of alcohol and a lipid with a base as a catalyst (Stavarache et al, 2005). A variety of lipids such as soybean oil, sunflower oil, canola oil, palmitic oil and different types of alcohols such as methanol, ethanol with bases such as KOH, and NaOH as a catalyst, have been studied (Dennis et al., 2010).

When the curves of transesterification reaction kinetics are evaluated, three regions can be observed (Noureddini & Zhu, 1997). In the first region, the kinetic is controlled by mass transfer; the second region is controlled by the reaction, and the third one is the

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equilibrium region. The mass transfer rate is mainly dependent on the processes of droplet breakage and coalescence, which are controlled by the droplet size distribution and flow structure. Kinetic modeling and mixing effects on the methanolysis process have been studied by different researchers (Noureddini & Zhu, 1997; Noureddini et al., 1998; Freedman et al. 1986; Stiefel & Dassori 2009; Leevijit et al., 2008; Ma et al., 1999). Freedman et al (1986) investigated the esterification modeling of soybean oil and the effect of mixing on the oil methanolysis at different alcohol/oil molar ratios. Their results show that at 30:1 alcohol/oil molar ratio, temperature of 60°C, and 0.5 wt% of NaOBu (Butyl Hydroxide Sodium) as a catalyst, reaction rate constants have values in the range of 11-26625 min^{-1}. The rate constants for 1 wt% concentration of catalyst are in the range of 7-3822 min^{-1}. Noureddini & Zhu (1997) studied the kinetics of esterification process and agitation effect of the reaction mixture of soybean oil and methanol with NaOH as a catalyst using a mechanical stirrer. Their results indicated that rate constants of transesterification reactions, at 50 ^{0}C and 300 rpm have values in the range of 0.007-1.228 s.mole/lit. They also obtained the reaction conversion at 150, 300 and 600 rpm, temperature of 50 ^{0}C, and the maximum conversion has been reported as 78, 80 and 92% respectively. Noureddini et al. (1998) also investigated the kinetics of a continuous process, with a motionless and high shear mixer. Their developed process resulted in a high conversion of vegetable oil to methyl ester. Stiefel & Dassori (2009) studied the kinetics of biodiesel production from soybean oil and methanol in a

continuous process including change of mixing pattern. They compared the results for the plug flow and CSTR reactors and concluded that plug flow pattern shows a distinctive benefit in terms of yields and reactor volume reduction in comparison to complete mixing. Leevijit et al. (2008) considered the effect of agitation on the yield of biodiesel production. Based on their studies, yield of methyl ester production was increased from 20 wt% to 90 wt% when the agitation is used for the reaction. Ma et al. (1999) studied the effect of agitation on beef tallow methanolysis. They studied Misek's equation on the droplet sizes and found that droplet size changes with $n^{-1.2}$ for beef tallow in methanolysis reaction.
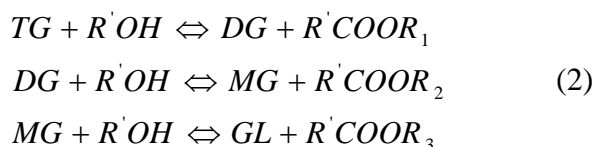
2. Theoretical section

Stamenkovic et al. (2007) studied the agitation effects on the methanolysis reaction of sunflower oil. They considered Sauter mean droplet size d_{32} as the mean droplet size d_p. Sauter mean droplet size is calculated from the following equation:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{1}$$

Where d_i is the drop diameter and n_i is the number of drops with a diameter d_i. They obtained a correlation in the form of $d_{23} = kn^b$ for the droplet sizes change with stirrer speed (Stamenkovic et al., 2007). A three-step mechanism has been proposed for the methanolysis process by most of the researchers in the literature (Noureddini & Zhu, 1997; Noureddini et al., 1998; Freedman et al. 1986). One molecule of Tri-

glyceride is converted to three methyl ester molecules and a glycerol in three stepwise reactions as shown in equation (2). However, this mechanism is rather hard to solve and is used in the reactor design applications.

$$TG + R^{'}OH \Leftrightarrow DG + R^{'}COOR_1$$
$$DG + R^{'}OH \Leftrightarrow MG + R^{'}COOR_2 \qquad (2)$$
$$MG + R^{'}OH \Leftrightarrow GL + R^{'}COOR_3$$

It is assumed that the reaction occurs at the interfacial area of two phases. For the complete dispersion of the light phase in the heavy phase, the agitator speed has to be more than a special value which is called a critical speed (Wu et al., 2007). Different equations have been developed for the calculation of agitator speed of different geometries. Specific interfacial area with the assumption of spherical droplets is calculated from the following equation (Treybal,1980):

$$a = \frac{6\varphi}{d_p} \qquad (3)$$

Where $a(m^2/m^3)$ is specific interfacial area, φ is dispersed phase hold up, and $d_p(m)$ is the mean drop size. Mean droplet size is calculated from Misek's equation:

$$d_p = \frac{16.3\left(\dfrac{H}{D}\right)^{0.46} \sigma e^{(0.087D)}}{n^2 d^2 \rho_c} \qquad (4)$$

$d_p(m)$ is the mean drop size, $n(rpm)$ speed of agitator, $d(m)$ agitator diameter, $\rho_c(kg/m^3)$ continuous phase density, $\sigma(N/m)$ surface

tension, $D(m)$ reactor diameter, and $H(m)$ is the reactor depth.

Droplet sizes are related to the speed by n^{-2}. Some researchers reported the relation of droplet sizes with speed, which is expressed with $n^{-1.2}$ (Azbel & Cheremisinoff, 1983) and $n^{-1.825}$ (Stamenkovic et al., 2007).

Dispersed phase hold up, φ, is considered as the volume of methanol to the operational reactor volume. $\sigma(N/m)$ is obtained by Slinn & Kendall for the system of sunflower oil and methanol from the following equation (Slinn & Kendall, 2008):

$$\sigma = 10^{-7}[TG]^2 - 10^{-7}[TG] + 0.0003 \qquad (5)$$

[TG] is the concentration of tri-glyceride during the methanolysis reaction with the unit of kmole/m^3. Maximum diameter of droplets is calculated from the proposed equations. When shear forces from the agitator are equal to the surface tension of the drop, the drop will break (Baldyga, 1999).

The purpose of this work is to propose a modified second order reaction model for the conversion prediction of *TG* to methyl ester in the methanolysis process of sunflower oil. It must be noted that the experimental results in this study are only used for evaluating the effects of mixing at a temperature of 55°C. Calculation of rate constant and activation energy are based on the literature data.

3. Experimental work
3-1. Materials
Purified food grade sunflower oil and methanol have been purchased from a local supermarket. The free fatty acid content of sunflower oil based on the Iranian National Institute of Standards (INIS) is less than

0.02%. NaOH with a purity of 99.0% has been purchased from Merck. The kinematic viscosity and density of the oil have been measured by a viscometer and density meter (SVM-3000 a product of Anton Paar Company) to be 30.14 mm2/s and 0.905 kg/m3 respectively.

3-2.. Experimental conditions

Experimental runs were performed at 55°C with a warm bath to keep the temperature constant. Two mixing speeds; 300 rpm and 600 rpm have been tested. 200 gr of oil with alcohol to oil molar ratio equal to 6:1 was used in the experiments. At first, the alcohol was under agitation and heating then NaOH was added slowly. Because of mixing, NaOH solves in the alcohol. After 10 minutes, sunflower oil was added. Reaction starts just after adding sunflower oil. Time of the reaction is 120 minutes. Sufficient samples were taken during the reaction to record the concentration change of TG. When the sample was taken, the reaction was stopped by being put in water and ice bath.

3-3. Apparatus

A 500 ml glass reactor was used for the methanolysis reaction. Reaction volume is 410 ml. A concentric two flat-blade paddle with a diameter and width of blades of 75 and 25 mm was used for the mixing. A 500 W mixer apparatus was used for mixing of the reaction system.

3-4. Analysis

Analysis of Methyl ester concentration has been performed on a GC with the standard method of EN 14103 and internal standard of methyl heptadecanoate (Munari et al., 2007)

which was purchased from the chemical store at the university. GC model is CP3800, which is a product of the Variant Company. The Capillary column specification is 30mm×0.32m×32m with a film thickness of 0.25 µm, which has been specially designed for biodiesel fuel. Most of the properties of sunflower oil, as well as the biodiesel properties, were measured in the Laboratory of Renewable Energies in the Faculty of Agriculture, Tarbiat Modares University. Density and Viscosity of oil were measured by Viscometer & density meters, SVM-3000, which are products of the Anton Paar Company.

4. Results and discussion

A second order reaction model has been proposed by considering the interfacial effects. The droplet sizes were calculated from equation (4) and were inserted into equation (3) for the calculation of the interfacial area. When the reaction is a second order (the proposed model), the conversion and concentration of *TG* can be expressed as:

$$X_{TG} = 1 - \frac{1}{1 + kat[TG]_0} \tag{6}$$

$$[TG] = \frac{1}{(kat + 1/[TG]_0)} \tag{7}$$

$$X_{TG} = \frac{[ME]}{3[TG_0]} \tag{8}$$

In a system of a mixture of oil and alcohol without reaction, there is a power equation between the droplet sizes and the agitator speed (Azbel & Cheremisinoff, 1983). When

methyl ester is produced, interfacial tension and maximum droplet sizes are decreased. In fact, production of methyl ester causes surface tension forces to be decreased, but shear forces generated by the agitator are constant. Combination of equations 3 to equation 6 results in equation (9), which shows the conversion of TG based on the mixture of physical properties, such as density, viscosity, and specifications of the mixer such as a propeller diameter.

$$X = 1 - \left[\cfrac{1}{1 + 6kt[TG]_0[A] / \left[\rho_A \left(\cfrac{16.3 \left(\frac{H}{D} \right)^{0.46} \left(10^{-9}[TG]^2 - 10^{-9}[TG] + 0.0003 \right) e^{(0.087D)}}{n^2 d^2 \rho_c} \right) \right]} \right]$$

(9)

In equation (9), concentration of TG is calculated and used for next step time. Since small step times were chosen, it does not cause a significant error. A dimension of k is $m.mole^{-1}lit.s^{-1}$. Comparison of the experimental data taken from (Vicente et al., 2005) and the model values of TG conversion in the sunflower oil transesterification at 25°C and 300 rpm is shown in Fig. 1. In this situation the parameter of the model (rate constant of reaction) is equal to $k = 3 \times 10^{-5} m.mole^{-1}lit.s^{-1}$. As shown from the figure, the relative error of the theoretical model results is less than one percent. Fig. 2 shows the results of the proposed model compared to the experimental results of Vicente et al. (2005) at 65°C and 300 rpm. Rate constant calculated from the model is equal to $k = 9 \times 10^{-5} m.mole^{-1}lit.s^{-1}$. Three sets of data, which are taken from Stamenkovic et al.

(2008) are shown in Fig. (3) to Fig. (5). Their study has been done at the lower temperatures such as 10°C, 20°C and 30°C and the results are presented in Table 1.
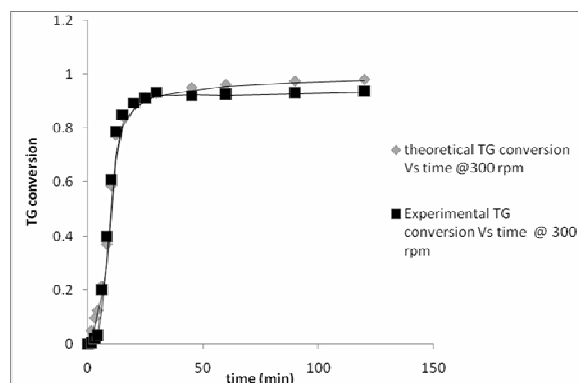

Figure 1. Comparison of experimental and theoretical TG conversion with *Vicente et al. (2005)* data at 25°C, 300 rpm and 6:1 alcohol to oil molar ratio, for Sunflower oil
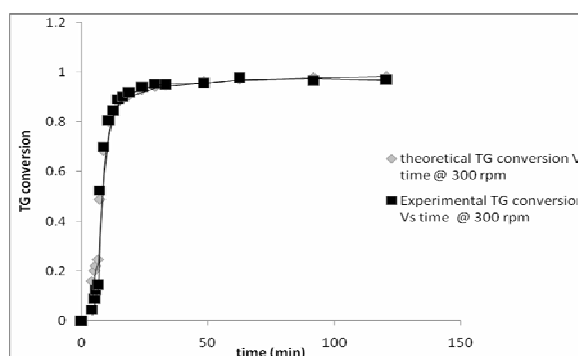

Figure 2. Comparison of the experimental TG conversion and theoretical values with *Vicente et al. (2005)* data at 65°C, 300 rpm and 6:1 alcohol to oil molar ratio.

Comparison of the model results with Noureddini & Zhu's (1997) data is shown in Figs. 6 and 7. Experimental values shown in Fig. 6 are for the transesterification of soybean oil at 50°C and 300 rpm.
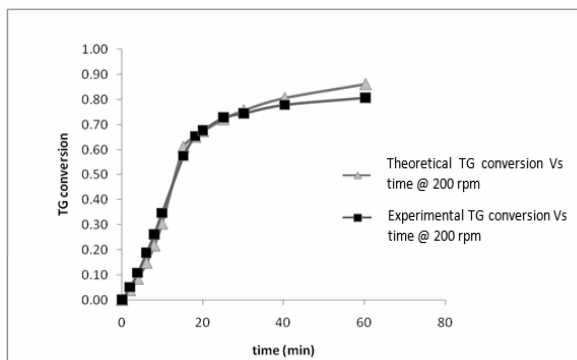
Figure 3. Comparison between theoretical and experimental values of TG conversion, using *Stamenkovic et al's. (2008)* study at 10°C, 200 rpm and 6:1 alcohol to oil molar ratio, for sunflower oil.
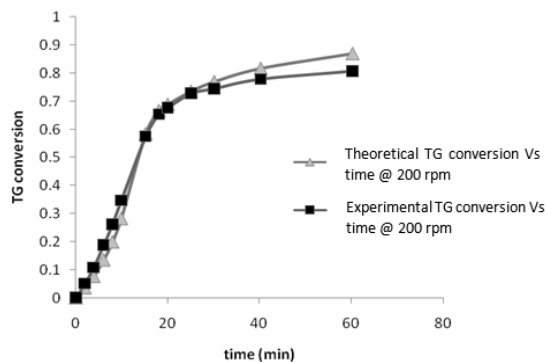
Table 1. Results of the model in abbreviation

	200 rpm	**300 rpm**	**600 rpm**
Sunflower oil @ 10°C	$k = 1.2 \times 10^{-5}$		
Sunflower oil @ 20°C	$k = 2 \times 10^{-5}$		
Sunflower oil @ 25°C		$k = 3 \times 10^{-5}$	
Sunflower oil @ 30°C	$k = 3.1 \times 10^{-5}$		
Sunflower oil @ 65°C		$k = 9 \times 10^{-5}$	
Soybean oil @ 50°C		$k = 2 \times 10^{-5}$	
Soybean oil @ 50°C			$k = 3.3 \times 10^{-5}$

Figure 4. Comparison between theoretical and experimental values of TG conversion, using the *Stamenkovic et al. (2008)* study at 20°C, 200 rpm and 6:1 alcohol to oil molar ratio, for sunflower oil.
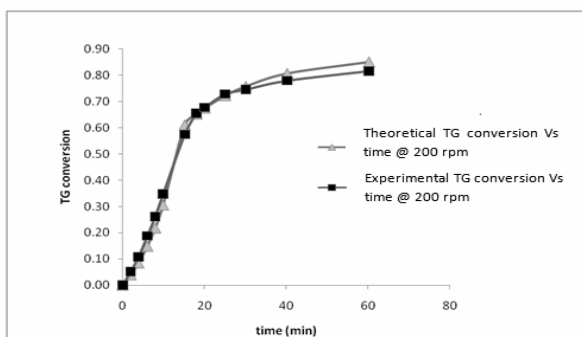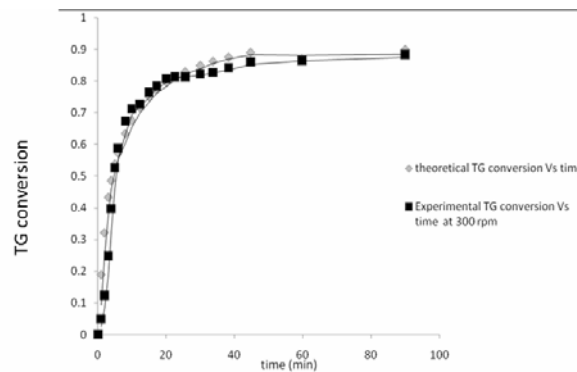

Figure 6. Examination of the model with the experimental data of *Noureddini & Zhu (1997)* at 300 rpm, 50°C and 6:1 alcohol to oil molar ratio.
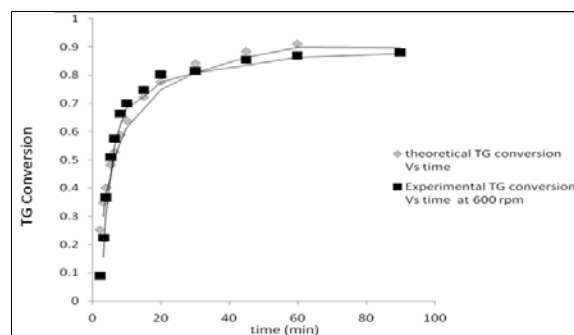

Figure 7. Comparison of the theoretical and experimental data of *Noureddini & Zhu (1997)* at 600 rpm, 50°C and 6:1 alcohol to oil molar ratio.

Figure 5. Comparison between theoretical and experimental values of TG conversion, using *Stamenkovic et al. (2008)* study at 30°C, 200 rpm and 6:1 alcohol to oil molar ratio, for sunflower oil.

Since equation (5) is for the system of sunflower and methanol, some modifications are required if it is used for the soybean oil.

Therefore it has been modified by trial and error to the following equation for soybean oil and methanol system:

$$\sigma = 10^{-9}[TG]^2 - 10^{-9}[TG] + 0.0003 \qquad (10)$$

From Stamenkovic et al's. (2007) data, the Misek's equation has been modified by changing its speed order for soybean oil. Based on the Stamenkovic et al (2007) experimental work, the order of the agitation speed was obtained for five different speeds and was extrapolated for 300 and 600 rpm. Azbel equation (Azbel & Cheremisinoff, 1983) was also varied for every speed. These modifications are reported in Table (2). The order of modification is obtained from the extrapolation of the data given in Table (2). Summation of the absolute error of this model is 1.93%. Rate constants calculated from data at 50^0C and 300 and 600 rpm are equal to 2×10^{-5} $m.mole^{-1}lit.s^{-1}$ and 3.3×10^{-5} $m.mole^{-1}lit.s^{-1}$ respectively. When more agitation speed is used, smaller drop sizes are generated and interfacial area increases and reaction speed increases.

Table 2. Determination of order of agitation at each speed with data taken from *Stamenkovic et al. (2007).*

n (rpm)	$d_{p_{exp}}$ (mm)	$d_{p_{theo}}$ (mm)	Order of speed
136.4	0.548	0.5731	-1.15
150.3	0.470	0.4487	-1.13
163	0.369	0.3906	-1.18
175.2	0.332	0.3253	-1.2
192.1	0.236	0.2507	-1.27
300	NA	0.1436	-1.3
600	NA	0.143	-1.33

The higher speed of agitation results in a shorter reaction time due to the generation of smaller droplets at a greater speed. At the interface of two phases, interfacial area plays an important rule. When the agitation speed increases, due to the increase in diameter of droplets, the interfacial area increases and the rate of reaction also increases. Reduction of droplet size with an increase of speed does not continue until the end of the reaction. During the reaction, the interfacial area of two phases changes with methyl ester production and is reduced during the reaction. After a few minutes, it reaches to a constant value, and this is when the droplet sizes no longer reduce.

4-1. Experimental results
In the experimental section, two different mixing intensities and their effect on methyl ester production have been examined (Fig. 8). It is clear from the curves that, higher mixing intensity has no significant effect on the methyl ester production. Since the experiment is performed at 55°C -close to methanol boiling point- it can be concluded that the parameter of model (k) approaches the rate constant of the reaction. In the other words, since the reaction happens in the interface of two phases, doing experiments at temperatures such as 55°C makes mass transfer resistance negligible and its kinetic depends only on the temperature.
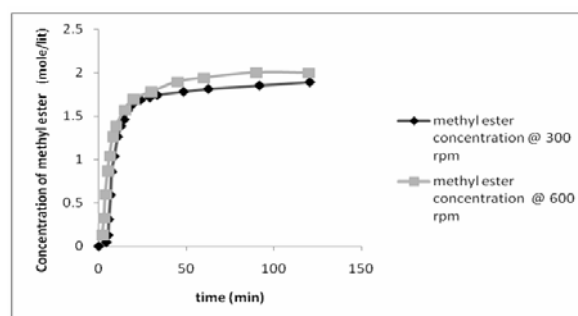

Figure 8. Methyl ester concentration produced from sunflower oil.

4-2. Activation energy calculation

Using five sets of data about Sunflower oil transesterification, and a ln(k) vs. 1/T plot (Fig. 9), dependency of the rate constants to the temperature was observed for Sunflower oil methanolysis. Data has been fitted linearly very well. Value of E/R has been obtained equal to 3390K. Value of the activation energy can be calculated with respect to the value of R (universal gas constant). Also, pre-exponential factor is equal to 2.201.
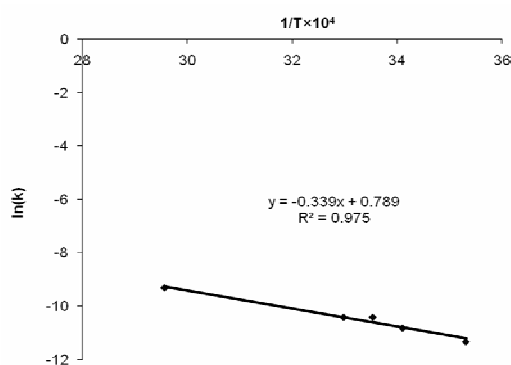

Figure 9. Temperature dependency of rate constant.

5. Conclusions

A kinetic model has been proposed to predict the TG conversion when the interfacial effects are presented and is used for the design of the methanolysis reactor. Other models reported in the literature include 6 differential equations that need to be solved simultaneously. The proposed model predicts acceptable results for sunflower oil, with no modification. But for soybean oil, the equation for the calculation of droplet sizes had to be modified. From the results, it is concluded that the parameter of the model, k, depends on temperature as well as agitation intensity, however, its dependency to the agitation speed is more significant at the lower temperatures. Due to the second order mechanism modifications, it is possible that other major parameters such as alcohol/oil molar ratio and catalyst concentration also affect the parameter of the model. The model produces more accurate results at lower temperatures due to the contribution of mass transfer effects vs. temperatures in the model.

Nomenclature

X_{tg} Tri-glyceride conversion

a interfacial area, m^2

φ dispersed phase hold up

$d_{p_{exp}}$ experimental measured values of droplet sizes, m

$d_{p_{theo}}$ theoretical measured values of droplet sizes, m

d_{32} Sauter mean droplet size, m

H reactor depth, m

D reactor diameter, m

σ interfacial tension, N/m

n agitator speed, rpm

d agitator diameter, mm

ρ_d dispersed phase density, kg/m^3

ρ_c continuous phase density, kg/m^3

ρ_e emulsion density, kg/m^3

[ME]   methyl ester concentration

$[TG]$ triglyceride concentration

$TG_.$ initial concentration of triglyceride

k parameter of the model (rate constant)

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