

SADIA NASREEN<sup>1,2</sup>  
HUI LIU<sup>1</sup>  
IVANA LUKIC<sup>3</sup>  
LIAQAT ALI QURASHI<sup>2</sup>  
DEJAN SKALA<sup>3</sup>

<sup>1</sup>State Key Laboratory of Biogeology and Environmental Geology and School of Environmental Studies, China University of Geosciences, Wuhan, PR China

<sup>2</sup>Department of Environmental Engineering, University of Engineering and Technology (UET), Taxilla, Pakistan

<sup>3</sup>University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

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## HETEROGENEOUS KINETICS OF VEGETABLE OIL TRANSESTERIFICATION AT HIGH TEMPERATURE

### Article Highlights

- Kinetics of transesterification catalyzed by different catalysts from literature was analyzed
- Transition and earth metals as catalyst for the high temperature transesterification
- Three kinetic models were used for predicting the effect of high temperature transesterification
- Apparent reaction rate constant and other parameters for more complicated models were determined

### Abstract

Currently, the catalytic efficiency and reusability of the solid base catalysts cannot meet the demand of industrial biodiesel production under low temperature. The purpose of this study is to define the kinetics of heterogeneous transesterification process that could be used for the prediction of the biodiesel synthesis at high temperature and pressure. The focus in this study was paid to recently reported data obtained with different catalysts used for biodiesel synthesis in a batch reactor at high temperatures. It was shown that three kinetic models, including: a) irreversible first order reaction, b) reaction with changeable order and c) resistances of mass transfer and chemical reaction at active sites of the catalyst, could be applied for predicting the effect of high temperature of the transesterification. The apparent reaction rate constant of the irreversible first order reaction was determined, as well as the parameters of the other two, more complicated kinetic models. The best agreement was obtained with the more complicated models and the mean relative percent deviation between calculated and experimentally determined triacylglycerols conversion for these kinetic models is between 3 and 10%.

*Keywords:* biodiesel, heterogeneous catalyst, kinetics, transesterification.

The most of biodiesel fuel is synthesized by homogeneous transesterification using alkaline catalysts and methanol (so-called homogeneous biodiesel synthesis). However, the costs of biodiesel production using homogeneous base or acid catalysts and environmental concerns resulting from the usually applied esters washing step, including the neutralization of residual homogeneous catalyst and the removal of soap and glycerol, have initiated the

search for more environmentally friendly processes based on the solid catalysts application. Therefore, the need for replacing the homogeneous with heterogeneous catalysts in transesterification and esterification of triacylglycerols (TG) was of high concern and many investigations were directed towards finding an effective solid catalyst that could be applied under the moderate reaction conditions. In principle, this could reduce the cost of biodiesel production, as it eliminates the need of numerous downstream processing steps, which cause the additional costs of biodiesel synthesis.

A large number of solid catalysts such as alkali earth and transition metal oxides, metal oxides doped with rare earth metals, zeolites and modified zeolites,

Correspondence: D. Skala, University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia.

E-mail: skala@tmf.bg.ac.rs; skala.dejan@gmail.com

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hydrotalcites, metals or oxides loaded on supports etc. have been investigated as catalysts for biodiesel production. Many biodiesel synthesis research studies in the past were focused on exploring the new and stable solid base catalysts that could be used at high temperature. In addition, it is believed that solid base catalysts have a strong potential to replace liquid acid catalysts. Although almost all of the reported studies could be separated into the transesterification realized at a low temperature (LTT), it seems that the full activity of rare metal catalysts could be obtained only by conducting the transesterification under a high temperature (HTT). In this study, a review of catalysts containing transition metals, lanthanides and actinides tested in transesterification of different vegetable oils at higher temperature is reported.

Recently reported data related to the kinetics of transesterification over solid catalysts were most often based on LTT and only limited information could be found about the kinetics of transesterification process at high temperature. Thus, the goal of this study was to analyze the results from literature for several catalysts (La/Mn [1], Ce/Mn [2], Sr/cinder [3], Fe-Zn double-metal cyanide (DMC) complex [4],  $\text{La}_2\text{O}_3/\text{ZrO}_2$  [5]) used in the HTT and to determine the most suitable kinetic model for representing a biodiesel synthesis under subcritical condition for methanol.

#### **Review of transition metals, lanthanide, actinide and their derivatives activity as catalyst for biodiesel synthesis**

Transition metals exhibit variable Lewis acidity, as well as various oxidation states and ion radius size. Due to these specific characteristics, many transition metal oxides and chlorides have widely been examined for different reactions and among them also for biodiesel synthesis by vegetable oils transesterification [6]. For example, molybdenum- and tungsten-containing solids have been reported in a number of reactions in which the acidity profile plays an important role in the reactions of isomerization, cyclic alkene oxidation, alcohol dehydration and vegetable oils transesterification [7].

It seems that solid acid catalysts are more effective under severe condition of transesterification (HTT), compared to some base solid catalysts which usually show acceptable activity at lower and even ambient temperatures [8-11]. Activity of different catalysts, representing combination of manganese and rare earth metals like La/Mn [1] and Ce/Mn [2] or Sr (the alkaline earth metal) supported on cinder [3], was tested in the soybean oil transesterification with meth-

anol under subcritical conditions (HTT). It was observed that the TG conversion rapidly increased with increasing the reaction time from 30 to 60 min at 180 °C when La/Mn catalyst was used [1], after which the conversion kept rising slowly and reaching a plateau at about 99% after 90 min. With Ce/Mn catalyst, the TG conversion was increased to 98.9% after 40 min after reaching the isothermal reaction (140 °C), while the FAME yield was 74.7% [2]. The transesterification reaction over Sr-cinder catalyst indicated that the TG conversion remarkably increased from 82.9 to 99.7%, and FAME yield from 77.1 to 90.6%, when the reaction time was prolonged from 30 to 60 min [3]. The change of both the TG conversion and the FAME yield was not observed after 60 min at 180 °C.

There have been several reports on the usage of transition metals like tin oxide or zirconium sulphate [12,13]. The acidity of zirconium sulphate could be also promoted by addition of tungstate sulphate [13]. In spite of the acidity effect, the reported data indicated that sulfated zirconia is a more active catalyst for transesterification of vegetable oils than the mixture of tungsten and zirconium sulphate [13].

Many studies were focused on the analysis of Zn, which also belongs to the group of transition metals, as a suitable catalyst for biodiesel synthesis. Thus, Zinc (II) Schiff base complexes were reported as suitable catalysts for biodiesel production from waste vegetable oil. Zinc oxide supported on alumina is capable of catalyzing the transesterification of plant oil under subcritical conditions of methanol [14] or in combination with some other alkaline metals at moderate conditions [15,16].

Some of the published studies showed that transition and other rare earth metals in combination mainly with some alkaline metals also possessed catalytic activity for biodiesel synthesis at the temperature close or little bit above the boiling temperature of methanol [17-30].

A review of reported studies with different catalysts containing transition metals, lanthanides and actinides, which are tested at higher temperature, is shown in Table 1.

Most transition metals are expensive and the catalysts prepared from them could be active only at high temperature and pressure necessary to achieve a high conversion of TG. It was found that pure ZnO and ZnO mixed with some other metal oxides exhibited the conversion efficiency ranging from 90 to 95% at high and low temperature, respectively [42,43]. Strontium loaded at fly ash, ZnO/La<sub>2</sub>O<sub>3</sub> and Zn/Al<sub>2</sub>O<sub>3</sub> have been also tested as catalysts for the transesterification of vegetable oil. The activity of zir-

Table 1. FAME yield obtained in the process of vegetable oil transesterification with transition metals, lanthanides and actinides used as solid catalyst

Catalyst	Time, h	T/ °C	Yield, %	Reference
WO <sub>3</sub> /ZrO <sub>2</sub> /MCM-41	2.5	200	85	[31]
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /ZrO <sub>2</sub>	10	200	77	[32]
ZrO <sub>2</sub>	1	200	64.5	[33]
ZnO/Al <sub>2</sub> O <sub>3</sub>	0.5	200	99	[34]
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub>	3	180	65	[35]
MnO/TiO	0.35	260	92	[36]
Fe/Zn	5	170	99	[4]
ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	-	250	97	[37]
TiO <sub>2</sub> /ZrO <sub>2</sub>	4	250	95	[37]
WO <sub>3</sub> /ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Continuo	250	90	[37]
VOPO <sub>4</sub> ·2H <sub>2</sub> O	1	150	80	[38]
WO <sub>3</sub> /ZrO <sub>2</sub>	5	200	97	[39]
La <sub>2</sub> O <sub>3</sub>	2	200	97.5	[40]
MnCeO <sub>x</sub>	5	140	87	[41]
La <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	5	200	96	[5]

conium oxide with tungsten oxide was also investigated [44,45].

A variety of transition metal-based solid acids like WO<sub>3</sub>/ZrO<sub>2</sub>, SO<sub>4</sub>/ZrO<sub>2</sub>, SO<sub>4</sub>/TiO<sub>2</sub> and SO<sub>4</sub>/ZrO<sub>2</sub><sup>-</sup>/Al<sub>2</sub>O<sub>3</sub> have already been tested for their catalytic efficiency in the process of free fatty acid esterification and TG transesterification [46-48]. Microwave heating in conjunction with heterogeneous barium, alumina, silica, zinc aluminate, and zirconium-based catalysts showed also a good catalytic activity for biodiesel production [49-51]. The sulfated transition metal oxides such as SO<sub>4</sub>/TiO<sub>2</sub>, SO<sub>4</sub>/ZrO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub><sup>+</sup>Fe<sub>3</sub>O<sub>4</sub> and SO<sub>4</sub>/SnO<sub>2</sub> were also reported in the literature as good catalysts [52-54].

The heteropoly tungstate (an acid solid catalyst) was active as a catalyst for esterification and transesterification reactions of waste and virgin vegetable oils. Commonly, heterogeneous heteropoly acids (HPAs) can be prepared by dispersing the HPAs on the high surface area supports such as hydrous zirconia (ZrO<sub>2</sub>), silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>). HPAs supported on high surface area supports such as Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup> were found useful in various acid catalyzed reactions [55].

It was reported that Cs<sup>+</sup> possessed high surface area and exhibited significantly higher activities than the parent heteropoly compound and other solid acid catalysts. In addition, the heterogeneous HPAs can facilitate much easier separation and reuse of the catalyst in the new batch. Application of solid HPAs for biodiesel synthesis using waste oils has been rarely reported. The activity of HPA catalysts are in the

following order: sHPW > 20% WO<sub>3</sub>/ZrO<sub>2</sub> > 20% HPW/Al<sub>2</sub>O<sub>3</sub> > 20% HPW/ZrO<sub>2</sub> > 20% HPW/SiO<sub>2</sub> [56,57].

The use of other transition metals such as zirconium, hafnium and antimonial-based catalysts for transesterification has also been studied [58,59]. The transesterification reaction over a Fe-Zn catalyst, performed at 170 °C, with the alcohol to oil mole ratio of 15:1 and 3 wt.% of catalyst, reached the oil conversion of 99% within 5 h. The catalyst activity was attributed to the Lewis acid active sites of probably Zn<sup>2+</sup> on the catalyst surface [4]. A vanadium phosphate solid acid catalyst was used in the transesterification of soybean oil, where the yield of methyl esters at 150 °C was 80% in 1 h [60].

The simultaneous esterification and transesterification of waste cooking oil was observed using the solid catalyst ZnO-La<sub>2</sub>O<sub>3</sub>, which combined acid (ZnO) and base sites (La<sub>2</sub>O<sub>3</sub>). Calcium oxide modified with lanthanum (La<sub>3</sub>O<sub>3</sub>/CaO) was effective for the transesterification at 65 °C giving the biodiesel yield of 94.1% within 1 h [61,62].

An investigation of La<sub>2</sub>O<sub>3</sub> catalyst was focused on the analysis of relation between its activity and basicity. At the highest temperature of 200 °C the FAME yield was 97.5% in 2 h. A novel solid super base Eu<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> complex was also used as catalyst for the transesterification of TGs with alcohols at 195 °C, which led to the TG conversion of 63.2% within 8 h [5,63].

#### Kinetic models used for heterogeneously catalyzed transesterification of vegetable oil

Various kinetic models have been used to describe the kinetics of heterogeneously catalyzed trans-

esterification. The most frequently used is a simple pseudo-first order kinetic model with respect to triacylglycerols [64-73]. An irreversible and reversible pseudo second-order kinetic model was used for transesterification of different oils [74-77], and the rate of the transesterification reaction was also fitted using a power law type kinetics model [78-81]. Kouzu *et al.* [82] reported that reaction kinetics varied from the zero order to first order with respect to TGs during the progress of FAME synthesis. Veljković *et al.* [83] proposed a pseudo-first order kinetic model for the transesterification of sunflower oil which includes mass transfer limitations, but with two separate correlations for mass transfer- and reaction rate-controlled stages. This model was successfully employed by Stamenković *et al.* [84] and Deshmane and Adeyuyi [85]. The models proposed by Liu *et al.* [86] and Huang *et al.* [87] consist of two and three different equations for different stages of the transesterification process. Some more complex models were developed based on the Eley-Rideal or Langmuir-Hinshelwood reaction mechanism [66,80,88-90], while other complex models consist of three [91] and four [92] consecutive and reversible second-order reactions.

Two kinetic models that have been recently proposed [93-95] predict well the reaction rate during the whole course of methanolysis process but for process realized at temperature below 100 °C. The model of Lukic *et al.* [93,94] has successfully been used by Sánchez *et al.* [96] for describing the kinetics of jojoba oil methanolysis over mussel shell-CaO and verified by Miladinovic *et al.* [97] for several calcium-based catalysts applied at low temperatures. The kinetic model of Miladinović *et al.* [95] was proved to be suitable for describing the kinetics of sunflower oil methanolysis catalyzed by CaO-based palm kernel shell

biochar [98] and some other calcium-based catalysts [99] at 60 °C.

The kinetics of transesterification at high temperature reported in literature always involved a simple first order (irreversible or reversible) [11,100-104] or *n*-order kinetic model [77,100], as it can be seen in Table 2.

### Models used for the analysis of HTT

Three different kinetic models are used as base points in this research: a) the simple pseudo-first order reaction model [64-73], which has been widely applied for defining the kinetics of transesterification at high temperature (Table 2), b) the kinetic model proposed by Miladinović *et al.* [95] (signed as MM model) and c) the kinetic model developed by Lukić *et al.* [93,94] (signed as IL model). Both MM and IL models were originally used for the prediction of TG conversion at lower temperatures, so the intention of this study was to check the possibility of using these models at higher temperature, too.

The simple pseudo-first model can be expressed as:

$$-\frac{dc_{TG}}{dt} = kc_{TG} \quad (1)$$

where  $c_{TG}$  is TG concentration and  $k$ , the reaction rate constant for the first order irreversible kinetic model.

Since the TG concentration is related to the TG conversion degree,  $x_{TG}$ , as follows:

$$c_{TG} = c_{TG0}(1 - x_{TG}) \quad (2)$$

Eq. (1) can be transformed into:

$$-\frac{dx_{TG}}{dt} = k(1 - x_{TG}) \quad (3)$$

Table 2. Kinetic of high temperature transesterification - literature review

Catalyst	Reaction condition				Kinetic model	Ref.
	<i>T</i> / °C	Mole ratio MeOH/oil	Catalyst amount, %	Stirring intensity, min <sup>-1</sup>		
CaO	215	6:1	2		Pseudo-first respect to MeOH	[101]
CaO/Al <sub>2</sub> O <sub>3</sub>	125-200	9:1	3	500	Pseudo-first	[102]
nano-MgO	200-260	36:1	3	1000	Pseudo-first	[103]
MgO, PbO, Mn <sub>2</sub> O	215	6:1	2		Pseudo-first	[101]
12-TPA/Nb <sub>2</sub> O <sub>5</sub>	150-225	18:1	3	600	Pseudo-first	[104]
Na <sub>3</sub> PO <sub>4</sub>	190-250	18:1	1	600	Pseudo-first	[105]
ZnO on an Al/Si support	200	30:1	2	300	First-order irreversible and reversible	[14]
Na/La	215	7:1	2		1 with respect to TG and 2 with respect to MeOH	[102]
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	90-150	12:1	8g		1.1	[77]

The MM kinetic model, proposed for the sunflower oil methanolysis catalyzed by quicklime, includes the changing reaction mechanism. This model assumes that the reaction rate with respect to TG is of zero order at high TG concentrations (the initial reaction period) and of the first order at low TG concentrations (the later part of the reaction). It is expressed as follows:

$$\frac{dx_{TG}}{dt} = k_m \frac{(1-x_{TG})(c_{R0} + 3c_{TG0}x_{TG})}{K + c_{TG0}(1-x_{TG})} \quad (4)$$

where  $k_m$  is the apparent reaction rate constant,  $c_{R0}$  is the hypothetical initial FAME concentration corresponding to the initial available active catalyst surface,  $c_{TG0}$  is the initial TG concentration and  $K$  is the model parameter defining the TG affinity for the catalyst active sites.

According to the IL model, which was previously developed for the methanolysis of sunflower and used vegetable oil in the presence of CaO-ZnO catalyst [93,94], the rate of methanolysis may be presented as the irreversible pseudo-first order reaction with the variable apparent rate constant,  $k_{app}$ , which takes into account the overall volumetric mass transfer coefficient of TG from oil to methanol phase,  $k_{mt,TG}$ , and the effective pseudo first-order reaction rate constant,  $k$ .

$$\begin{aligned} \frac{dx_{TG}}{dt} &= k_{app}(1-x_{TG}) = \frac{k_{mt,TG}k}{k_{mt,TG} + k}(1-x_{TG}) = \\ &= \frac{k(k_{mt,TG})_0 \left[ 1 + \alpha x_{TG}^\beta \right]}{k + (k_{mt,TG})_0 \left[ 1 + \alpha x_{TG}^\beta \right]} (1-x_{TG}) \end{aligned} \quad (5)$$

where  $(k_{mt,TG})_0$  is the overall volumetric mass transfer coefficient at the beginning of the process, depends on interfacial area between the oil and methanol,  $a_0$ , and  $\alpha$  and  $\beta$  are fitting parameters. The interfacial area changes with the TG conversion according to the proposed correlation:

$$\frac{a}{a_0} = 1 + \alpha x_{TG}^\beta \quad (6)$$

Since:

$$\frac{1}{k_{mt,TG}} = \frac{a_0}{a(k_{mt,TG})_0} \quad (7)$$

then  $k_{mt,TG}$ , which defines the rate of mass transfer, depends on the interfacial area and the proposed correlation assumes that it is also a function of TG conversion:

$$k_{mt,TG} = (k_{mt,TG})_0 \left[ 1 + \alpha x_{TG}^\beta \right] \quad (8)$$

For the purpose of simulation and modeling of  $x_{TG}$  versus time, Polymath Educational 6.10 software was used. The significance of the kinetic models was statistically evaluated using the mean relative percent deviation (MRPD) between the experimentally determined and predicted TG conversions:

$$MRPD = \frac{100}{n} \sum_1^n \left| \frac{x_{TG_{mod}} - x_{TG_{exp}}}{x_{TG_{exp}}} \right| \quad (9)$$

#### Determination of kinetic parameters and simulation of TG conversion

The kinetics was analyzed using results reported in literature for transesterification of vegetable oils catalyzed by 5 different catalysts [1-5]. The effect of the reaction temperature on the transesterification efficiency when these catalysts were used is presented in Figure 1. In the transesterification of soybean oil catalyzed by the La/Mn catalyst, it was observed that TG conversion significantly increased from 18.0 to 99.0% when the reaction temperature increased from 60 to 180 °C [1]. When Sr-cinder was used as a catalyst, the TG conversion increased from 63.3 to 99.7% when the reaction temperature increased from 90 to 180 °C [3]. In both cases, further increase of temperature above 180 °C did not considerably change the TG conversion. More severe change in TG conversion was observed with Fe-Zn DMC [4] and La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> [5] used for transesterification of high-acid-value oil or sunflower oil, respectively. Authors of these investigations reported that conversion of triacylglycerols changed from 2% at 100 °C to 97% at 160 °C after 8 h of reaction [4], and from 4% at 60 °C to 96% at 200 °C after 5 h of reaction [5]. The results of Ce/Mn-catalyzed transesterification indicated that the reaction rate was slow at 120 °C, with a TG conversion of only 48% after 1 h of process [2]. However, the increase in temperature to 140 °C led to the increase of the TG conversion up to 98.9% after 1 h [2]. A further increase of the reaction temperature has only minor effect on the TG conversion. It was interesting to notice that the experimental data for La/Mn, Sr/cinder, Ce/Mn and La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts indicated that during the transesterification process the transformation of triacylglycerols into FAME was not completed although the TG conversion was almost 100%. Namely, the FAME yield for all four catalysts were about and below 90% (Sr/cinder, Ce/Mn and La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts) and little bit higher (La/Mn catalyst). For Fe-Zn DMC data of FAME yield were not available.

The simple first order kinetics of TG conversion, Eq. (3), was used to calculate the reaction rate cons-

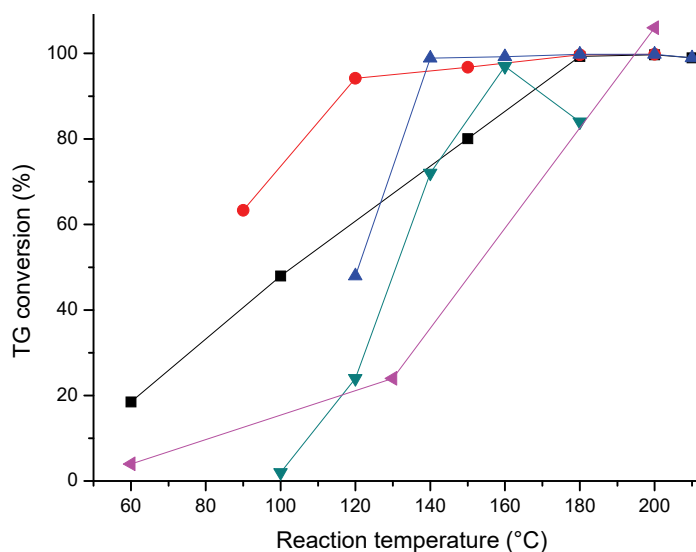


Figure 1. Effect of reaction temperature on TG conversion and FAME yield using: La/Mn [1] (■); Sr-cinder [3] (●) Ce/Mn catalyst [2] (▲); Fe-Zn DMC [4] (▼); La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> [5] (◄).

tant,  $k$ , at different temperatures. The obtained  $k$  values were analyzed using the Arrhenius plot of  $\ln k$  versus  $1/T$  (Figure 2) in order to estimate the activation energy ( $E_a$ ) and the pre-exponential factor ( $A$ ).

The defined temperature dependency of the reaction rate constant was used for modeling and simulating the TG conversion *versus* time at the isothermal condition as well as at different temperatures applying all three kinetic models (I order, MM and IL). The MM and IL model parameters were then optimized to give the minimal MRPD. The determined parameters of three kinetic models are shown in Table 3. TG conversion at various reaction times was calculated by Eqs. (3)–(5) for the I order, MM and IL models, respectively using corresponding parameters from Table 3. The predicted TG conversion is compared to the experimentally determined one in Figure 3.

The IL [93] and MM [95] models gave a better agreement, compared to the simple irreversible first order reaction model. The average agreements between experimental and calculated TG conversions are shown in Table 4.

The prediction of TG conversion achieved at different temperatures was the best with the first order reaction model (the average MRPD for five catalysts was about  $\pm 13\%$ ), while it was less good with the other two models (MM model about  $\pm 23\%$  and for IL model about  $\pm 14\%$ ; Table 4). It is reasonable because the influence of TG conversion at different temperature and determination corresponding parameters (the activation energy and frequency factor of transesterification process) was based on this simple model, and then this relationship between,  $k$ , the

reaction rate constant and temperature was also applied for other two models [93,95]. It was only possible to be done, because the more complex MM [95] and IL [93] models do not give the possibility for a simple calculation of the relationship between the apparent reaction rate constant and temperature. However, the simulation of TG conversion at the isothermal condition was much better with the MM and IL models (the average MRPD for five catalysts was 2.7 and 3.5%, respectively) and with the I order model it was 11%.

However, it should be noted that the Arrhenius plot for Ce/Mn catalyst was questionable (Figure 3c) because the data of TG conversion obtained at higher temperature were almost the same and very close to 100%. Thus, data corresponding to temperature below 160 °C must only be taken into account for prediction the Arrhenius plot and determination the activation energy and the frequency factor of the transesterification process. Further problems in analyzing experimental data at different temperatures arise from the realization of transesterification in the batch reactor. Namely, for reaching a desired temperature of isothermal operation, and especially when it is higher than 100–120 °C, some time for heating the reaction mixture is usually required. During that period, so called non-isothermal operation of transesterification is realized, and thus the conversion obtained at some isothermal condition, *e.g.*, at 180 °C, is represented as a summation of conversions obtained during heating period up to 180 °C (it is almost 1 h) and after 1 h of the isothermal process at that temperature. For such simulation and calculation TG conversion during

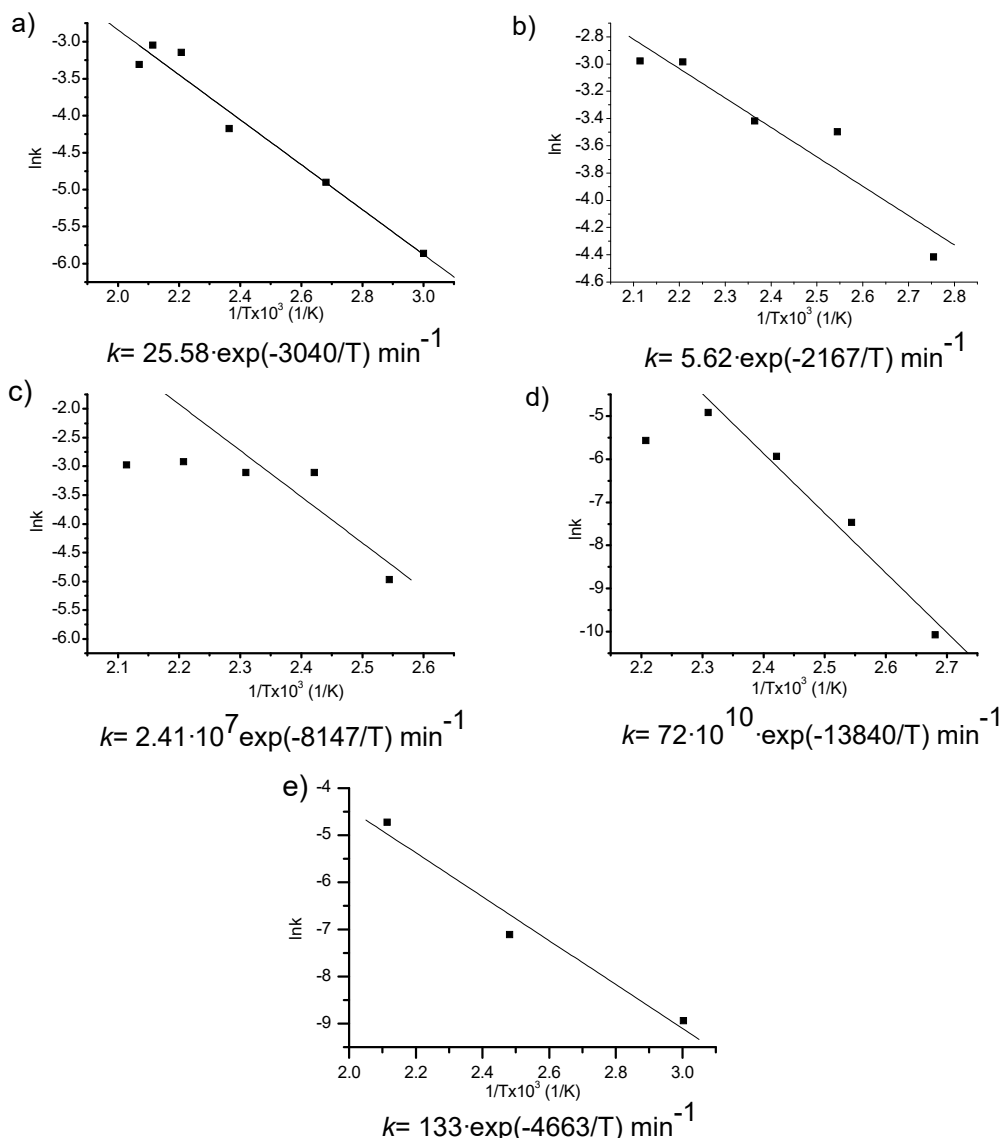


Figure 2. The temperature dependency of the reaction rate constant determined using the 1 order reaction model for: a) La/Mn [1]; b) Sr-cinder [3]; c) Ce/Mn [2]; d) Fe-Zn DMC [4] and e)  $\text{La}_2\text{O}_3/\text{ZrO}_2$  [5].

Table 3. Determined parameters for three kinetic models used for simulation of transesterification process performed with different catalysts

Catalyst	MM model [95]			IL model [93]			
	$k / \text{min}^{-1}$	$c_{R0} / \text{mol dm}^{-3}$	$K / \text{mol dm}^{-3}$	$k / \text{min}^{-1}$	$k_{mt,0} / \text{min}^{-1}$	$\alpha$	$\beta$
La/Mn	Figure 3	0.58	1.5	Figure 3	0.052	5.2	1.1
Sr-cinder		0.065	1.15		0.007	310	4.2
Ce/Mn		0.58	1.55		0.038	16	2.1
Fe-Zn DMC		1.88	3.15		0.0069	16	1.1
$\text{La}_2\text{O}_3/\text{ZrO}_2$		0.9	1.2		0.0068	150	1.1

Table 4. Comparison of different models used for calculation TG conversion and experimental data defined as MRPD (%) by Eq. (9)

Catalyst	Temperature range, °C	First order reaction	MM model [95]	IL model [93]
La/Mn	60-210	13.0	21.7	3.4
Sr/cinder	90-200	4.1	38.9	16.9
Ce/Mn	120-200	13.0	10.9	13.1

Table 4. Continued

Catalyst	Temperature range, °C	First order reaction	MM model [95]	IL model [93]
Fe-Zn DMC	100-180	16.5	25.6	17.0
La <sub>2</sub> O <sub>3</sub> / ZrO <sub>2</sub>	60-200	19.6	19.1	18.7
La/Mn	isothermal 180 °C	14.9	1.4	3.0
Sr/cinder	isothermal 180 °C	12.1	5.3	7.1
Ce/Mn	isothermal 140 °C	14.9	0.7	0.3
Fe-Zn DMC	isothermal 160 °C	6.4	3.7	2.0
La <sub>2</sub> O <sub>3</sub> / ZrO <sub>2</sub>	isothermal 200 °C	6.4	2.6	5.2

the non-isothermal+isothermal transesterification, the relationship between the reaction rate constant and temperature is necessary, as well as the initial TG conversion after reaching the desired temperature of isothermal operation. This procedure of calculating the TG conversion at isothermal operation was applied and the data are presented in Figure 3. As shown by the *MRPD*-values and the curves (Figure 3), it is clear that the more complex MM [95] and IL [93] models gave a better simulation of isothermal operation for all

five catalysts. These models, which are defined by several parameters and not only by the *k* value as for the I order model, gave the possibility of fine tuning the experimental curves and good agreement to the experimental data.

Finally, it was shown that metal oxides from this group of metals (transition metals, the rare earths metals) might be used for biodiesel synthesis only at higher temperature. However, their possible dissolution into different phases of reaction mixture (FAME,

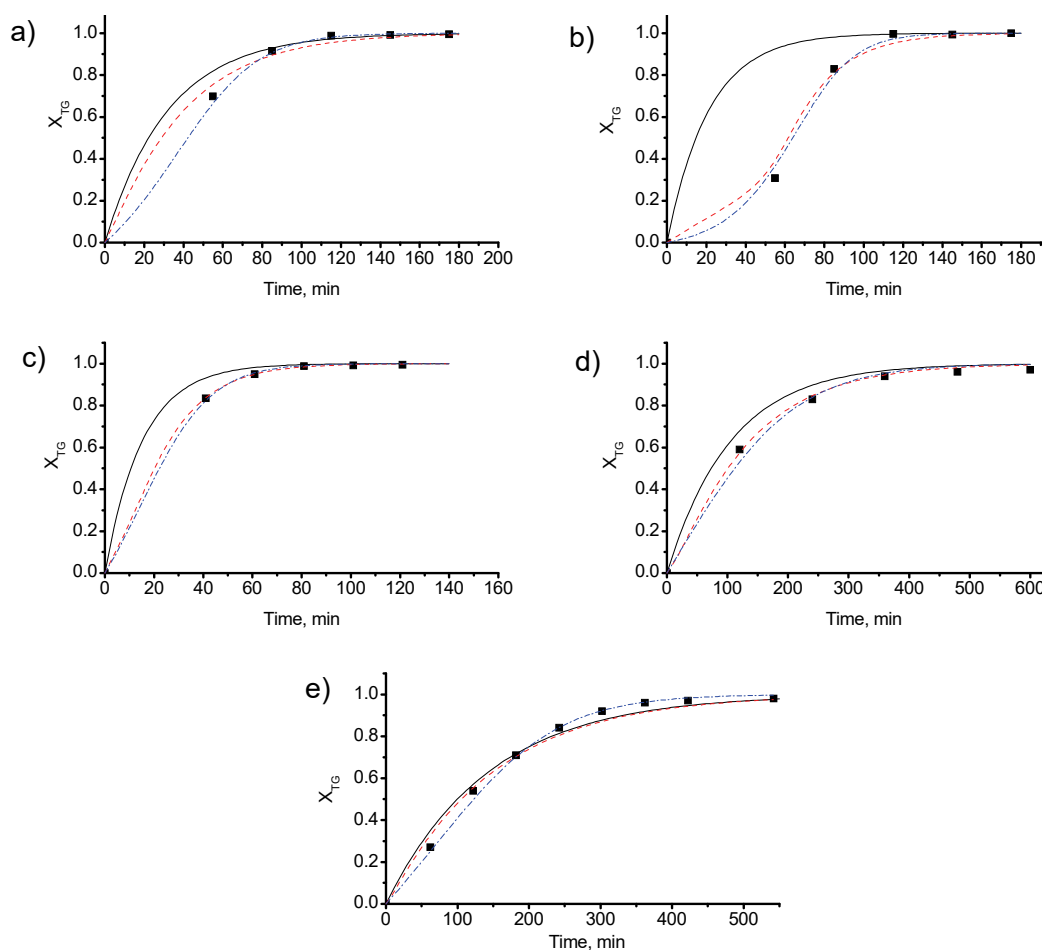


Figure 3. Comparison of calculated using different kinetic models and experimentally determined (■) TG conversion using: – first order reaction kinetic model; --- IL kinetic model [93] and - - - MM kinetic model [95] for transesterification catalyzed by: a) La/Mn [1], b) Sr-cinder [3], c) Ce/Mn [2], d) Fe-Zn DMC [4] and e) La<sub>2</sub>O<sub>3</sub>/ ZrO<sub>2</sub> [5] catalyst.



glycerol, excess of methanol) must be taken into account, and also must be determined to what extent the non-catalyzed transesterification with subcritical methanol could be expressed. According to the experimental data analyzed in this study, the non-catalyzed reaction is obviously not so important for the Ce/Mn catalyst. Namely, the rate of transesterification process over the Ce/Mn catalyst was very fast at 120–140 °C, but it was not in the case of the La/Mn or Sr/cinder catalysts which had optimal activity at 180 °C.

The phase composition under the subcritical condition of methanol, and its dependence on the presence of solid catalyst, is also very important and must be analyzed or calculated. This can be done analyzing the phase composition in the presence of some inert solid particles with same physical characteristics as catalyst and comparing to phase composition without presence of solid phase. Taking into account the possible influence of solid phase on the rate of transesterification process it seems that the IL model is more realistic for defining the physical meaning of models parameters [93].

## CONCLUSION

Metal oxides from the group of transition metals as well as some from the group of earth metal could be successfully applied as catalysts for biodiesel synthesis at higher temperature. Usually conditions belonging to high temperature transesterification (above 140 °C, pressure above 2 MPa) correspond to subcritical condition of methanol in which the non-catalyzed but very slow transesterification is also possible. The presence of such catalyst, and in this study, the five different types were analyzed, La/Mn, Sr/cinder, Ce/Mn, Fe-Zn DMC and La<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>, increases the rate of transesterification. Three different kinetic models were analyzed for prediction of triacylglycerols conversion *versus* time for isothermal transesterification. Simulation curves and calculation of the average percent relative deviation showed that complex models based on changeable reaction rate orders, or models based on the change of resistances to mass transfer of triglycerols from oil phase to active sites of catalyst which are defined with several parameters, gave better calculated TG conversion compared to simple 1<sup>st</sup> order kinetic model.

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SADIA NASREEN<sup>1,2</sup>  
 HUI LIU<sup>1</sup>  
 IVANA LUKIC<sup>3</sup>  
 LIAQAT ALI QURASHI<sup>2</sup>  
 DEJAN SKALA<sup>3</sup>

<sup>1</sup>State Key Laboratory of Biogeology and Environmental Geology and School of Environmental Studies, China University of Geosciences, Wuhan, PR China

<sup>2</sup>Department of Environmental Engineering, University of Engineering and Technology (UET), Taxilla, Pakistan

<sup>3</sup>Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Karnegijeva 4, 11000 Beograd, Srbija

NAUČNI RAD

## KINETIKA HETEROGENO KATALIZOVANE TRANSESTERIFIKACIJE BILJNIH ULJA NA VISOKIM TEMPERATURAMA

*Trenutno stanje istraživanja pokazuje da katalitička aktivnost i mogućnost višestrukog korišćenja čvrstih baznih katalizatora ne može da zadovolji potrebe i zahteve za primenu ovih katalizatora za sintezu biodizela na niskim temperaturama. Cilj istraživanja primenjen u ovom radu je definisanje kinetike heterogeno katalizovane transesterifikacije uz mogućnost izračunavanja efekta sinteze biodizela na visokim temperaturama i pritiscima. Za to su upotrebljeni, nedavno objavljeni u literaturi, rezultati ispitivanja sinteze biodizela u šaržnim uslovima na visokim temperaturama koji su realizovani uz primenu različitih čvrstih katalizatora. Analizirani su sledeći kinetički modeli procesa sinteze biodizela definisani kao: a) nepovratna reakcija I reda; b) reakcija sa promenljivim redom i c) postojanje otpora za prenos mase i hemijske reakcije na aktivnim centrima katalizatora koji definišu brzinu procesa. Svi ovi modeli mogu da se iskoriste za proračun efekta transesterifikacije triacilglicerola (ulja) na visokoj temperaturi. Prividna konstanta brzine u slučaju primene najjednostavnijeg modela (a, nepovratna reakcija I reda) je određena, kao i ostali parametri složenijih modela (b, odnosno c). Najbolje slaganje eksperimentalno određenih i izračunatih stepena konverzije triacilglicerola (od 3 do 10%) postiže se primenom složenijih kinetičkih modela.*

*Ključne reči: biodizel, heterogeni katalizatori, kinetika, transesterifikacija.*