

Researches Regarding Biodiesel Synthesis

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This study dealt with the reaction kinetics of rapeseed oil transesterification with methyl alcohol, temperature, reactants molar ratio and catalyst amount influences upon triglycerides conversion. It was found out that increasing temperature and decreasing alcohol: oil ratio lowered triglycerides final conversion. Reaction rate is increasing with increasing temperature and catalyst amount. On the other hand increasing catalyst amount in reactants mixture also leads to a greater quantity of soap formation, detrimental to biodiesel yield. Kinetic experiments performed at 6:1 methanol : oil molar ratio, 50 and 60 °C reaction temperatures, 0.3% and 0.6% (by weight of reactants) catalyst loading, showed that during the first part, reaction evolved far from chemical equilibrium and on that time frame (0÷30 min) it is proved a second – order kinetics. Also in the same time, reaction rate constant doubles its value at a 10 °C temperature increase and is 2^{1/2} times higher when catalyst load doubles.

Key words : biodiesel, fatty acids methyl esters, transesterification, rapeseed oil

Energy production without using fossil fuels is an intensively discussed matter nowadays. Solar energy can be recovered not only in its pure representation as radiations, but also as wind or stored in living organisms as tissues and spare substances where from is possible to be recovered by burning those compounds. The biodiesel production by triglycerides transesterification with low molecular weight alcohols is in the same line as well.

The biodiesel production has been applied worldwide. In spite of this fact, researchers work to find innovative solutions to improve manufacturing technologies so far known.

Among the most remarkable studies on this matter were those accomplished by Freedman and coworkers [1], on soybean oil transesterification. Authors ascertained that soybean oil transesterification evolves through consecutive, reversible reactions. Forward reaction is of pseudo-one kinetic order at bigger alcohol to oil ratios (30:1) and is of second order at smaller ratios, backward reaction evolving at second kinetic order. Activation energy for forward reaction and backward reaction were found out to be in different conditions between 8 and 20 kcal / mol.

Nouredin and Zhu [2] investigated the effect of agitation on methanolysis of soybean oil working with Reynolds numbers between 3000 and 18600 and finding out that agitation speed influenced conversion until Reynolds number reached a value of 12400.

Kusdiana and Saka [3] carried out a study of rapeseed oil transesterification with supercritical methanol. They discovered that methyl esters content to a certain reaction time increases with the raise in the methanol: oil ratio and temperature. They also ascertained that oil transesterification with supercritical methanol is of first kinetic order, as a function of the concentration of triglycerides including mono-, diglycerides and free fatty acids as well.

Darnoko and Cheryan [4] reported that at 50÷60 °C, 6:1 methanol: oil molar ratio and 1% potassium hydroxide as catalyst, the reaction appeared to be of second kinetic order up to 30 minutes reaction time, after that it seems to evolve like a first or zero kinetic order reaction. On their opinion, the temperature has a little but noticeable effect. The

optimum catalyst concentration is 1%. Instead, to a catalyst concentration below 0.5% there was a delay in methyl ester production, followed by a rapid increase of the reaction rate after 6 min. Authors suggested that a two-phase reaction mixture explains the delay by a slower mass transfer when the mixing is not so strongly.

Theerayut and others [5] studied transesterification of the palm oil with methanol in the presence of sodium hydroxide catalyst to a 6:1 methanol :oil molar ratio, 60 °C temperature, and 2000 Reynolds number for stirring. Experimental data verified a second kinetic order mathematical model for the reaction. A stronger stirring can eliminate slower increasing of the methyl esters at the beginning of the reaction because of a poorer diffusion between the two phases (oil-alcohol). All three steps of the forward reaction (tri-, di-, mono-glycerides transesterification) are more important than the backward reaction and the overall reaction evolves with great speed to methyl esters production whose highest equilibrium concentration is 99.1%.

Another paper [6] reported studies on sunflower oil methanolysis with sodium hydroxide as catalyst. Methanolysis was carried out at different agitation speeds (200÷600 rpm). Mass-transfer limitation was effectively minimized at stirring speed of 400÷600 rpm with no delay period. Lowering the temperature resulted in a fall in the reaction rate, prolonging the reaction time necessary to achieve maximum production of methyl ester. Using 0.5% sodium hydroxide catalyst proved to be adequate, resulting in 97÷98% conversion. A 6:1 methanol : oil molar ratio led to a 97.5÷97.7% conversion, but increasing this ratio beyond 6:1 tended to speed up the reaction and to increase the final amount of the methyl esters. However, increasing methanol to oil ratio calls for an increase in equipment dimensions. Experimental data proved a second-order of the reaction rate expression.

The present work dealt with rapeseed oil methanolysis kinetics with sodium hydroxide as catalyst, advancing and checking a kinetic model. Temperature, reactants ratio and catalyst amount influences on reaction rate were studied. In the time frame when the reaction complies with second-order kinetics, reaction rate constants and activation

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energy were established. A mathematical correlation between reaction time and conversion was found as well.

Experimental part

Rapeseed oil triglycerides transesterification reaction with methanol was carried out mainly in a lab batch reactor equipped with stirrer and heating jacket. A heating circulator maintained desired temperature and this was monitored by an electronic thermometer with thermocouple probe.

Lab batch reactor characteristics were:

- inside diameter : 79.52 mm;
- reactor height : 187 mm;
- stirrer equipped with three propeller, each having two wings ($\varphi = 45^\circ$) on the same shaft;
- propellers diameter: 45 mm.

Experiments were conducted at 1000 rpm stirring speed. Extremely vigorous agitation (with splashing) allowed the reaction to evolve in the kinetically controlled region where diffusion phenomena did not influence on reaction rate. In other words, the conversion and time to reach maximum conversion were independent of further increase of stirring speed. Since it seems [5] the reaction takes place at the oil-alcohol interface, at least during the initial period when the two reactants have a limited miscibility, a strong mixing is of great importance.

Some of the experiments were conducted in a 60 L pilot batch reactor, fitted with blades propeller and steam heated jacket. Agitation speed was 120 rpm.

Raw filtered rapeseed oil, having an acidity index of $1.6 \div 2.9$ mg NaOH / g and maximum 750 ppm water content was used. Acidity was neutralized with a precise determined amount of NaOH added over catalytic necessities. Sodium hydroxide pellets were of analytical grade. Methanol used was of 99.85% concentration, technical grade with maximum 500 ppm water content.

In order to experiment, the batch reactor was filled with rapeseed oil, heated to reaction temperature, then the sodium hydroxide in methanol solution was quickly fed and the agitation was started. Samples to be analyzed were sometimes removed from biodiesel phase after the lapse of the reaction time and glycerol phase separation. For the kinetic determinations, samples ($1 \div 2$ mL each) were withdrawn from the reaction mixture at various intervals depending upon reaction conditions. The reaction was immediately "frozen", mixing samples with acetic acid solution in water and cooling them quickly.

Considering that experimentation and analyzing samples spend a lot of time and specific materials, it was tried a reduction of the experimental field by some preliminary tests. Thus, temperature and reactants ratio influence upon triglycerides conversion was studied first. Four synthesis experiments were conducted, three in a

60 L pilot batch reactor and one in a one-liter lab batch reactor. Catalyst amount influence upon biodiesel yield was also tested in two experiments in the lab batch reactor previously described.

Reaction kinetic features determination experiments were conducted to a 6:1 methanol: oil molar ratio since the literature on this matter and the preliminary tests, suggested that being the optimum reactants ratio in triglyceride transesterification. Catalyst amounts used were 0.3 and 0.6 % by weight of reactants. Experienced temperatures were 50 and 60°C.

Withdrawn samples at various intervals of time were analyzed to find out the amount of free glycerol (FG) and total glycerol (TG), used to evaluate conversion. The analysis procedure is known as "Total, Free and Combined Glycerol Iodometric-Periodic Acid Method" (similar to A.O.C.S. Ca 14-56 method).

Glycerol phase was analyzed for soaps and residual catalyst content using a two-step colorimetric titration with phenolphthalein and bromophenol blue as indicators and 0.1 N HCl solution as titrant. This last method is a modified version of A.O.C.S. Cc 14-79 method.

Results and discussions

Temperature and reactants ratio effect

Table 1 shows free and total glycerol amounts (wt. %) resulted in four experiments conducted in a pilot batch reactor and in a lab batch reactor, at two temperatures, two methanol : rapeseed oil molar ratios and the same reaction time (2 h).

Triglycerides conversion was calculated based on the following equation:

$$\%TriG \text{ conversion} = 100 - \frac{M_{oil}}{M_{glycerol}} (\%TG - \%FG) \quad (1)$$

where TriG stands for triglycerides, M_{oil} and $M_{glycerol}$ represent rapeseed oil respectively glycerol molecular weights, %TG and %FG stand for total glycerol respectively free glycerol percentage, both for biodiesel product obtained.

The equation (1) is not a rigorous one because the oil is considered to be formed from triglycerides exclusively and bound glycerol (BG = TG - FG) is considered to derive only from triglycerides, while biodiesel may contain mono- and di-glycerides in addition to triglycerides. However, using formula (1) offers a common ground to compare conversions in different working conditions.

As indicated in table 1, for 1 : 6 oil to methanol molar ratio, a bigger conversion is obtained than for 1 : 4 ratio. This fact is explained by chemical equilibrium displacement towards methyl esters formation when a larger excess of methanol is used. Furthermore, increasing

Parameters	Pilot batch reactor			Lab batch reactor
	1 / 6	1 / 4	1 / 6	
Oil / methanol molar ratio	1 / 6	1 / 4	1 / 6	1 / 6
Temperature (°C)	60	60	80	80
Catalyst amount (wt. %)	0.3	0.3	0.3	0.3
Free glycerol (wt. %)	0.004	0.0056	0.0033	0.038
Total glycerol (wt. %)	0.212	0.5586	0.508	0.7
Triglycerides conversion (wt. %)	98	94.7	95.16	93.65

Table 1
TEMPERATURE AND RAPESEED OIL:
METHANOL MOLAR RATIO INFLUENCE ON
TRIGLYCERIDES CONVERSION

the methanol excess beyond the usual amount makes more difficult glycerol phase separation from biodiesel phase, lowering the density gap between the two phases (the alcohol is distributed mainly in the glycerol phase). Besides, a higher alcohol excess involves an increase in equipment size both for main reaction and methanol recovery.

In addition, as listed in the same table, increasing the operating temperature leads to a smaller conversion. The explanation lies in the reaction exothermic effect (about -9 kcal/mol) and in accordance with Le Châtelier's Principle, reaction equilibrium constant moves down. Besides, Darnoko and Cheryan [4] assert that palm oil transesterification rate determined in a batch reactor, increase with the temperature until 60°C and further increase in temperature do not necessarily reduced time to reach maximum conversion. The same authors claim that below 50°C, increasing oil viscosity raise problems in pumping and stirring.

Between 50 and 65 °C temperature effect upon transesterification is small but noticeable.

Catalyst amount influence

Catalyst amount influence on biodiesel yields was studied by two experiments in lab scale batch reactor. The following working parameters were identical in the two experiments: temperature (60°C), rapeseed oil : methanol molar ratio (1 : 6), reaction time (2 h), stirring speed (1000 rpm). Oil and alcohol derived from the same recipients in both experiments. The only variable was the amount of sodium hydroxide catalyst that was calculated relative to the mass of all reactants. The necessary sodium hydroxide for the oil acidity neutralization was established and added separately. Results are presented in table 2.

As listed in table 2, using a greater amount of catalyst in biodiesel synthesis leads to less biodiesel and more soaps formation.

The addition of an excessive amount of catalyst with the purpose to increase reaction speed and to diminish reactor volume, give rise to the following effects beside that above mentioned :

- glycerol phase separation from biodiesel phase is hindered and that could evolve till the formation of gels at greater soaps contents;
- biodiesel washing difficulties because of high stability emulsions formation;
- biodiesel and glycerol phases purification is hampered, demanding greater devices with an increased energy consumption.

Consequently, the catalyst amount (sodium or potassium hydroxide / alcocide) recommended to be used is the lowest quantity providing reaction completion in an economic period of time. However, if the reaction speed is important and can lead to a reduction in reactor dimensions, to increasing productivity or to a continuous flow process, then the use of a greater catalyst amount might be an option.

Catalyst loading (%)	Biodiesel yield (%)	Triglycerides conversion (%)	Glycerol phase content of	
			NaOH (%)	Soap (%)
0.3	83.74	98.05	0.717	13.5
0.6	79.43	98.4	0.735	19.17

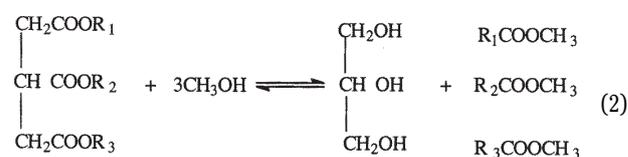
Table 2
EFFECT OF CATALYST LOADING ON
BIODIESEL YIELD

Reaction kinetics

In order to give a simple expression to the reaction rate as a variation of one of the reactants concentration with time, first it was set experimentally and by calculation, the volume variation during the reaction. Those works proved that the reaction products volume at the reaction end is lower by 2% at most than reactants volume at the reaction beginning. Reaction volume changing being very low and in order to simplify calculations, it was considered that reaction takes place without volume variation.

Some authors [2,4] proposed a three steps reaction kinetics, when triglycerides turns to diglycerides, the last ones turns to monoglycerides and finally this ones turns to fatty acids methyl esters (FAME) and glycerol, in reaction with methanol. Each step leads to a methylated compound molecule for each methanol molecule consumed in reaction. As a result it can be reported six reaction rate constant.

For a more simplified mathematical model, this paper considers only the overall reaction as is shown bellow:



Reaction rate constant can be determined from increasing content of FAME or glycerol formed after a period of time or alternatively from the decreasing content of one of the reactants.

It can be chosen to track the content of the unreacted compound (URC), when the expression of the reaction rate is $r = -d(\text{URC}) / dt$. If it is considered that URC concentration is proportional to bound glycerol content (BG), then it can be written: $r = -d[\text{BG}] / dt$. Also it can be chosen to track the glycerol content formed in reaction as free glycerol (FG). This time, the reaction rate expression will be: $r = d[\text{FG}] / dt$.

It will be presumed that the transesterification reaction is a bimolecular reaction of second overall kinetic order, similar to esterification and esters hydrolysis reactions.

In this kinetic study, the conversion will be used as variable that is more convenient in engineering calculations than concentration [7].

Because the reaction rate depends on its stoichiometry and kinetics as well, the triglycerides methanolysis reaction will be expressed in the following form: $A + 3B = \text{products}$.

Conversion is defined as $X_{A_0} = (C_{A_0} - C_A) / C_{A_0}$ where C_{A_0} represent starting concentration of the component A and C_A is the concentration of the component A at the time "t".

Reaction rate equation is:

$$-r_A = -\left(\frac{dC_A}{dt}\right) = -\left(\frac{dC_B}{dt}\right) = kC_A C_B \quad (3)$$

Elapsing time “t”, the amount transformed from reactant A will be $C_{A_0} X_A$ and $C_{B_0} X_A = 3C_{A_0} X_A$ will be the amount transformed from reactant B, according to reaction stoichiometry. Reaction (3) will come to the following form:

$$-r_A = C_{A_0} \left(\frac{dX_A}{dt} \right) = k(C_{A_0} - C_{A_0} X_A)(C_{B_0} - 3C_{A_0} X_A) \quad (4)$$

If the reactants molar ratio is denoted as $M = (C_{B_0} / C_{A_0})$ then the equation (4) can be written as outlined below:

$$\left(\frac{dX_A}{dt} \right) = kC_{A_0} (1 - X_A)(M - 3X_A) \quad (5)$$

Integrated form of the above equation will be:

$$\frac{1}{C_{A_0}} * \frac{1}{M-3} * \ln \frac{M-3X_A}{M(1-X_A)} = kt \quad (M \neq 3) \quad (6)$$

If in the graphical representation of the left side of the equation (6) versus time, points given by the resulted pairs of values are found on a straight line passing through the axes origin, then the presumed kinetic model overlaps with the real model.

In figure 1 conversion variation versus time is represented, and in figure 2 kinetic equation graphical representation at different temperatures is given. From the last figure it can be observed that in its first part reaction evolves far away from equilibrium and graphical representation being a straight line the assumption made earlier that the reaction is of second global kinetic order in that area is accurate. Further, the reaction evolves near the equilibrium toward gradually it tends to. The form of the graphical representation changes likely due to the reverse reaction that increases in importance.

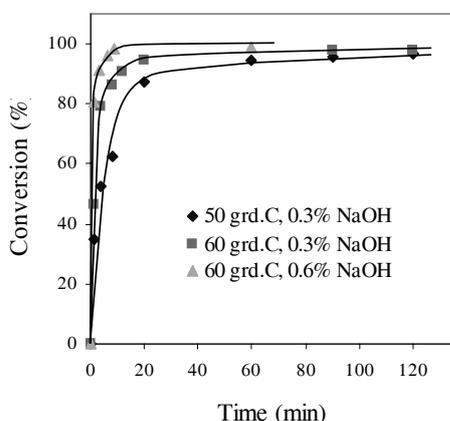


Fig. 1. Conversion variation vs. time

Reaction rate constant at different temperatures (table 3) can be determined from the linear section slope of the graph representation (fig. 2). The slope calculation on the linear section was made with LINEST statistics function that is relied on the least squares method, this function belonging to Microsoft Excel Program.

In table 3 it can be observed that an increase of ten degrees of temperature doubles reaction rate, while a two times increase in catalyst amount raises two and a half times transesterification reaction rate on linear section of the graph representation in figure 2. Those findings are valid as long as reaction is of second kinetic order

In figure 2, $C_{A_0} = 0.828$ and $M=6$.

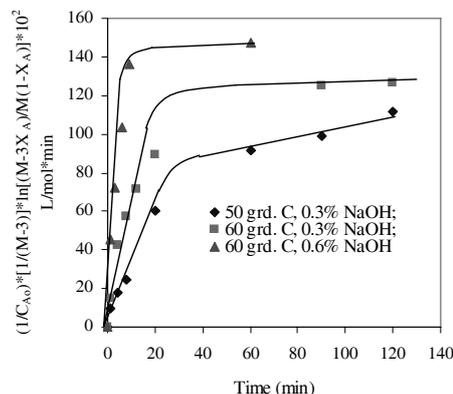


Fig.2. Kinetic equation (6) graphical representation for rape oil transesterification with methanol

Table 3
REACTION RATE CONSTANT

Temperature	Catalyst amount	Reaction rate constant
⁰ C	%	L/mol*min
50	0.3	$3.9 \cdot 10^{-2}$
60	0.3	$6.65 \cdot 10^{-2}$
60	0.6	$16.6 \cdot 10^{-2}$

The data in table 3 can also be used to establish the reaction activation energy with one of the two expressions below:

$$\ln k_T = \frac{10E}{RT(T+10)} \quad (7)$$

$$\alpha = \frac{RT^2 \ln 2}{E} \quad (8)$$

In these last expressions, “ k_T ” is the “reaction rate temperature coefficient” and shows how much the reaction rate increases to a 10 °C increase in temperature and “ α ” is the “reaction rate temperature gradient” and represents how many degrees must the temperature rise as the reaction rate doubles.

Activation energy for the transesterification reaction of triglycerides with methanol results from the equations (7) and (8) if “ k_T ” or “ α ” are replaced with their values obtained using data from table 3 and is equal to 69000 J / mol.

The most straightforward way to establish the necessary reaction time for a certain conversion, is the experimental method. Figure 1 depicts how this method works, experimental plots and curves in this graph giving indications about reaction evolution.

Also, using “Curve Expert” graphics program, it was found that a rational function of the following form:

$$y = \frac{a + bt}{1 + ct + dt^2} \quad (9)$$

where “y” and “t” represent the conversion respectively the reaction time, describes the best, conversion evolution versus time, as can be seen in figure 3, where the curve mathematically expressed by the equation (9) overlaps well over the experimental plots.

The above mentioned program calculates the coefficients a, b, c, d in equation (9) for the three curves shown in figure 1.

With the function (9) can be determined not only graphically but also by calculation the necessary reaction

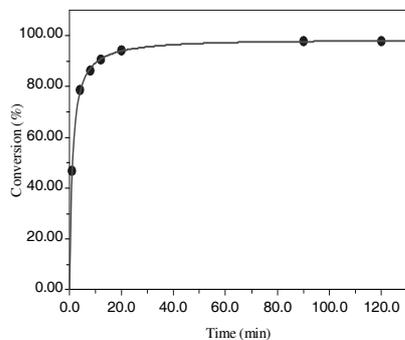


Fig. 3. Conversion vs. reaction time at 60 °C, 0.3% NaOH catalyst. Experimental plots and curve generated by "Curve Expert" Program

time under certain operating conditions to achieve the desired conversion.

Further, using this reaction time, the reactor volume is possible to be established for a certain input of a plant.

Conclusions

Working in the kinetic area where the reaction rate is not influenced any more of diffusion phenomena and using raw materials with very low water content, factors on which further depends the way the transesterification evolve are: reactants ratio, temperature, and catalyst amount.

Thus increasing methanol to oil molar ratio, increases conversion by shifting chemical equilibrium towards methyl esters formation.

Increasing reaction temperature increases reaction rate but also leads to a lower conversion. This latter fact is due to the exothermic nature of the transesterification reaction. According to Le Châtelier's Principle, an exothermic reaction is disadvantaged by increasing temperature.

Increasing the amount of catalyst used, significantly increases the reaction rate, but also lowers biodiesel yield while the amount of soaps formed grows, generating difficulties in subsequent biodiesel processing.

Biodiesel synthesis reaction by triglycerides transesterification with methanol in alkaline catalysis is of

second kinetic global order only in the time span 0÷30 min, function of reaction temperature and catalyst amount. Thus the higher temperature and catalyst amount, the more limited the time span when the reaction is of second kinetic order, will be.

A temperature rise of 10 °C doubles the reaction rate to the same concentration of catalyst. Doubling catalyst concentration at the same temperature, increases 2.5 times the reaction rate. These last conclusions are valid as long as reaction is of second kinetic order.

Activation energy of the triglycerides transesterification reaction with methanol, calculated from kinetic data in the time span when the reaction is of second kinetic order is of 69000 J/mol. This value is in satisfactory accordance with previously reported values by different authors.

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