



Kinetics of Rapeseed Oil Methanolysis in presence of KOH Catalyst – Studied with Gas Chromatography

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ABSTRACT

Kinetic study of methanolysis of rapeseed oil in two phase liquid-liquid systems is performed in a batch reactor observing substances concentration gradient for process optimization. Concentration of initial substances, temperature of the system and stirring speed have significant effect on transesterification of rapeseed oil. They are considered as dominant factors to be optimized. Transesterification mechanism is known to be mass-transfer and kinetically controlled. Based on this mechanism kinetic equations for the transesterification have been derived. Theoretical equations are in good agreement with the results obtained from experimental analysis. After experimental validation, simulation has been done over a wide range of transesterification duration for optimized temperature and stirring speed. Simulation results predicted that for optimized condition, it is possible to obtain higher biodiesel production in the transesterification process. Results from this study signify effect of rapeseed oil transesterification kinetics on biodiesel production. This batch process study can be applicable for flow through reactor performance prediction which will be helpful for industrial application of this technology.

Keywords: Biodiesel, kinetics, transesterification, rapeseed oil, gas chromatography

1. INTRODUCTION

Biodiesel production is one the technologies to solve the problem of depleting fossil fuel usage and green house effect. The ineffectiveness of today's conventional fossil fuel usage results occurrence of green house gases (GHGs) in the atmosphere. The potential risk of chronic accumulation to these GHGs in atmosphere has not been adequately addressed as of to date, but their effects on global warming are well known and there is ample evidence of their adverse effects in the atmosphere. Reaction kinetics of biodiesel production by transesterification in industrial scale is still under study. To solve this problem, kinetic study (i.e., reaction kinetics) of transesterification has been carried out by the authors [1-3]. They used edible oil and animal fat as a reactant by observing reactant's concentration gradient. However, they compromised by product formation, which is a very important for biodiesel standardization compliance. In course of transesterification, even though triglyceride consumed but at the same time intermediate by products are formed and decayed. This may be harmful for the biodiesel [4]. Because these intermediate by products have filter blocking tendency in fuel injection system [5]. A number of studies have been reported in published literature on factors affecting transesterification kinetics of biodiesel production. Effect of reactants composition on transesterification has been studied [6] by measuring substances composition remaining in batch reactor. It has been reported that methanol:oil = 9:1 molar ratio in presence of catalyst (KOH) has contributed optimal methyl ester yield. Also change in catalyst content and stirring speed with change in methyl ester yield has been documented. The same author also observed that increased catalyst content beyond 0.7

wt% has negligible effect on methyl ester yield which is a function of composition of substance remaining. Temperature is another dominant factor affecting transesterification kinetic [7]. It has been observed that kinetic coefficients of TG, DG and MG increase with increase in temperature from 50°C to 65°C, where KOH was used as a catalyst. This companion author used basic catalyst (KOH) but did not neutralize it to stop transesterification after desired duration. It has been revealed that with the increase in temperature, transesterification rate increases due to increase in transesterification kinetics. Moreover, laboratory study has shown that increasing temperature beyond 65°C has decreased ester yield. Because boiling point of methanol is 65°C [7]. If transesterification occurs at boiling temperature less reactant will be available to form desired product. Increasing temperature as well as stirring speed up to a saturation level has increased in rapeseed oil-methanol mass transfer and hence transesterification efficiency [8]. These companion authors have reported that 60°C temperature and 500 rpm stirring speed are optimum variables for rapeseed oil transesterification. Present work endeavors understanding rapeseed oil transesterification kinetics by lab scale experiment, development of kinetic equation describing transesterification, validation of theoretical equation by experimental data and optimization of conditions for the transesterification. These information will be helpful to develop model for plug flow transesterification reactor for industrial application of this transesterification technology.



2. PROBLEM DESCRIPTIONS

Issues need to be addressed in kinetic study of rapeseed oil transesterification process are: concentration of substances remaining, kinetic co-efficients of substances and process variables (i.e., temperature and stirring speed). These information are essential to fix optimum process conditions to achieve maximum rapeseed methyl ester formation. To get optimized process variables, Lab scale batch experimentation need to be carried out. Because batch process is superior to both plug flow and continuous operation [9]. It is suitable to determine reaction kinetics due to its flexibility over a wide range of process conditions. Moreover, flow-through reactor model can be developed using parameters (kinetics) independently determined from batch and semi-batch experiments [10]. As a result these optimized process variables will also be helpful to demonstrate continuous plug flow reactor performance prediction. This will foster industrial application of the transesterification technology for the optimum conversion of rapeseed methyl ester (i.e., biodiesel).

3. MATERIALS AND METHODS

3.1 Chemicals

Rapeseed oil (C18 ~ 96% and mostly triglyceride) was obtained from AAK's Rapeseed oil refinery located about 150 meter from RME production facility of Ecobrånse AB, Sweden. All chemicals used in the experiment such as methanol, potassium hydroxides and n-heptane were of analytical reagent (AR) grade. N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) of CAS #: 24589-78-4 was purchased from Sigma-Aldrich, Germany.

3.2 ASTM D6584/EN 14105 Standard Solutions

GC calibration solutions 1, 2, 3, 4, 5 (consist of different proportions of glycerol, triolein, 1-monooleoyl-rac-glycerol and 1, 3 - diolein), internal std #: 1 (butanetriol, CAS #: 42890-76-6) and internal std #: 2 (tricaprin, CAS #: 621-71-6) were purchased from SUPELCO, USA.

3.3 Methods

Rapeseed oil transesterification reaction in Batch process was carried out according to the standard method outlined in industrial Agricultural Products Center - Publications & Information described by F. Ma *et al.*, 1998 [3].

According to this method, transesterification was conducted in a 100 ml beaker. About 30 g Rapeseed oil and 6.9 g catalyzed methanol (3.75% KOH dissolved in CH₃OH) of Oil: Methanol

= 1:6.35 molar ratio were pre-heated to reaction temperature 60-65°C. The reactants were than mixed and allowed to react in 5-60 minutes. After each batch of reaction, catalyst (KOH) was neutralized with equivalent amount of H₃PO₄ (according to V₁.N₁=V₂.N₂ formula) to stop transesterification reaction. Subsequently the substances were also quenched at 0°C to stop any further alteration. Then 4 ml of each sample was taken in a 10 ml vial and washed with equal volume of water. After water wash each sample vial was centrifuged in 15 minutes for phase separation. Upper phase sample was taken and was analyzed for mono-glyceride (MG), di-glyceride (DG), tri-glyceride (TG), pH and water content. Each experimental cycle was repeated twice to ensure reproducibility

3.4 Product Analysis

Each batch of transesterifying sample was analyzed for TG, DG and MG by gas chromatography (GC); water content by METTLER TOLEDO DL39, Karl Fischer Coulometer and pH by HACH pH paper, 0-14 pH range. The composition of the methyl esters was analyzed by GC using a Agilent Technologies 789A GC - system equipped with a split injection system, a flame ionization detector and a Agilent ChemStation software were used. The column was a 15.0 m × 320 μm, and 0.1 μm capillary column with helium 99.9995% purity at 5.1414 ml/min as the carrier gas and split ratio of 100:1. Injector and detector temperatures were 250°C and 300°C. Oven temperature started at 50°C for 1 min, were increased to 180°C at a rate of 15°C/min, then were increased to 230°C at a rate of 7°C/min and finally were increased to 370°C at a rate of 10°C/min and held at this temperature for 5 min.

Analysis had been carried out by the GC column as specified above. First unbound hydroxyl groups of glycerine, mono- and diglycerides were silylated with N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) to convert into more volatile compounds prior to analysis. Two internal standards: 1,2,4-butanetriol for the determination of free glycerol and 1,2,3-tricaproyl glycerol (tricaprin) for the determination of glycerides were used in calibration process as well as for analysis. Calibration was accomplished with glycerol, 1-monooleoyl glycerol (monoolein), 1,3-dioleoyl glycerol (diolein) and 1,2,3-trioleoyl glycerol (triolein) as reference substances.

4. EXPERIMENTAL SETUP

Schematic diagram for Rapeseed Oil transesterification is shown in **Figure 1**. The system is equipped with a 100 ml beaker assembly, a thermometer, a piece of parafilm paper covering the beaker and the whole system is mounted onto a heating mantle (with magnetic stirrer @ 500 rpm) controlled by thermostat.

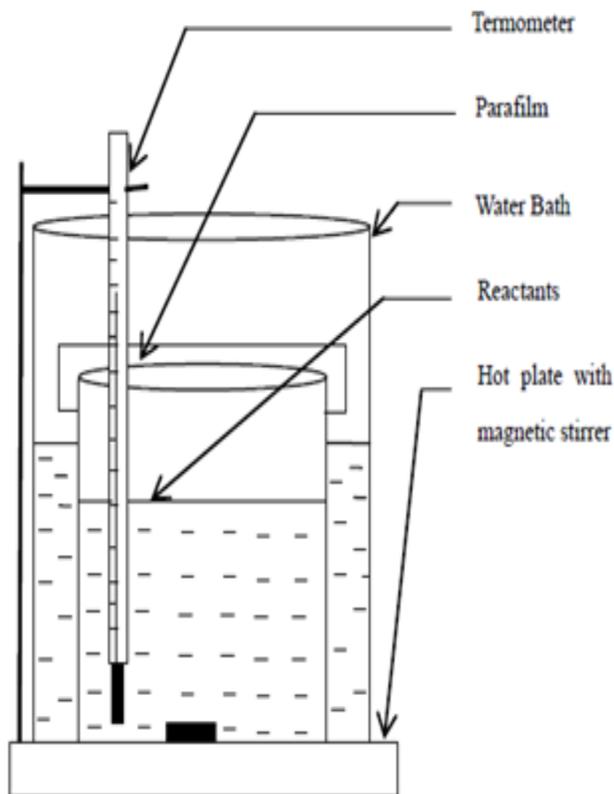


Figure 1: Schematic Diagram of Setup for Transesterification Process of Rapeseed Oil

Crude Rapeseed Oil and catalyzed CH_3OH is mixed intimately. Homogeneous liquid-liquid interfacial mass transfer is ensured by stirring action with magnetic stirrer which is further enhanced by application of heat. After predetermined transesterification duration, esterified substances were analyzed by mass measurement techniques as outlined in **subsection 3**.

5. THEORETICAL BACKGROUND

5.1 Reaction Mechanism

Batch transesterification reaction mechanism for liquid (rapeseed oil) – liquid (catalyzed methanol) two phase system can be described by both mass transfer and kinetics [8]. Triglyceride from bulk glyceride phase is transferred to: (i) liquid-liquid film interface, (ii) reacts at the interphase according to kinetics, (iii) products transfer back into bulk liquid phase. Constraints are resistance associated at the interphase (mass transfer controlled and kinetic controlled) and can be

characterized by concentration, mass transfer and kinetic coefficients of initial substances (i.e., triglyceride).

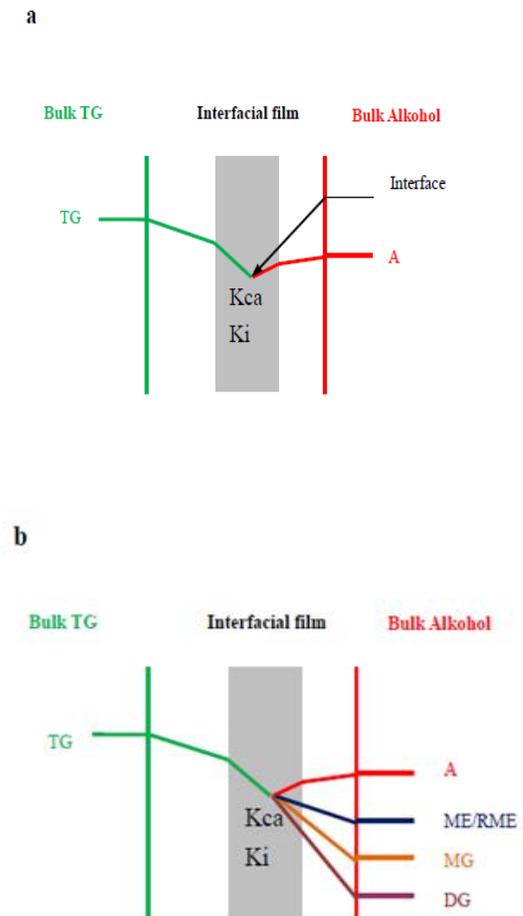
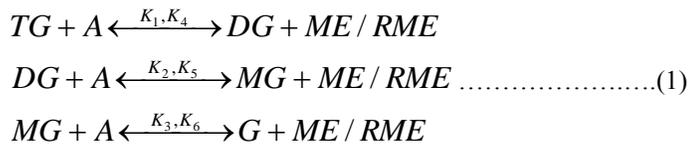


Figure 2: (a) Mass transfer coupled with reaction kinetics at liquid-liquid interface. (b) Evolution of transesterifying products.

Reaction kinetics is governed by the concentration of substances and their kinetic co-efficients as depicted in Figure 2a;b

5.2 Predictive Theories

According to reaction mechanism (**Figure 2**) and for the reaction kinetics transesterification of TG with methanol, in presence of alkaline catalyst gives rise esters of fatty acids and G. DG and MG are intermediates. Reaction steps are in Equation 1 where K_{1-6} are kinetic co-efficients. K_1, K_2, K_3 are the kinetic co-efficients for forward reactions and K_4, K_5, K_6 are the same for backward reactions respectively.



Generic set of rate equations taking into account mass transfer and stepwise reactions involved in the transesterification of TG is given in Equation 2.

$$\begin{aligned}
 \frac{d[TG]}{dt} &= K_c a([TG]_i - [TG]) - K_1[TG][A] + K_4[DG][ME] \\
 \frac{d[DG]}{dt} &= K_1[TG][A] - K_2[DG][A] - K_4[DG][ME] + \\
 &K_5[MG][ME] \\
 \frac{d[MG]}{dt} &= K_2[DG][A] - K_3[MG][A] - K_5[MG][ME] + \\
 &K_6[G][ME] \\
 \frac{d[G]}{dt} &= K_3[MG][A] - K_6[G][ME] \\
 \frac{d[A]}{dt} &= -K_1[TG][A] - K_2[DG][A] - K_3[MG][A] + \\
 &K_4[DG][ME] + K_5[MG][ME] + K_6[G][ME] \\
 \frac{d[ME]}{dt} &= K_1[TG][A] + K_2[DG][A] + K_3[MG][A] - \\
 &K_4[DG][ME] - K_5[MG][ME] - K_6[G][ME] \\
 \dots\dots\dots(2)
 \end{aligned}$$

5.3 Numerical Solution

POLYMATH 6.10 build 261 software was used to solve ordinary differential equations described in Equation (2). Corresponding B.Cs were set and validation was accomplished by curve fitting. Experimental validation turns out values of kinetic co-efficients in Equation 2.

Once empirical values of kinetic co-efficients are established (unique for the system), the system is simulation for a range of operating conditions. This gives a flexible dynamic simulation for the transesterification process.

6. RESULTS AND DISCUSSION

6.1 Factors Affecting Transesterification

The present study focused on monitoring dynamics of transesterification process at optimized process condition, i.e., 60-65°C and 500 rpm [8]. These are dominant factors affecting transesterification. It has been observed that above 65°C ester yield decreased as explained in section 1.

6.1.1 Dynamics of Transesterification

Batch process demonstrated dynamics of transesterification in 0-60 min. Dynamic composition profile of transesterifying substances is presented in Figure 3 (quantification is accomplished on the basis of MG, DG and TG). This figure showed rapid decline of TG resulting equivalent production of RME. Sigmoid curves for the evolution of MG and DG are also revealed from this figure. This indicated the low reaction rate or the delay at the beginning (for MG and DG) 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. These phenomena (mass transfer and kinetics controlled) are nicely depicted in the Figure 3 and briefly discussed in reaction mechanism sub-section. Property of transesterifying substances is given in Table 1.

6.1.2 Effect of Temperature

Transesterification involved reaction between two immiscible phases – rapeseed oil and methanol phase. Optimized transesterification temperature is reported to be 50-65°C [7]. Within these temperatures, effect of phase resistances reduced where lower viscosity and weak liquid (rapeseed oil) – liquid (catalyzed methanol) phase boundary enhance rapeseed oil – methanol mass transfer. This mass transfer is further enhanced by the application of stirring speed @ 500 rpm. As a result faster RME conversion is achieved within these reaction temperatures. As mentioned before 65°C is the boiling temperature of one of the reactants (methanol). So transesterification temperature should be precisely controlled to avoid this overheating.

6.1.3 Effect of Water Content

Batch experiment showed that transesterification produced 150-274 ppm of water in 0-60 min. This water formation inhibited RME formation [11]. As a result after 15 min, composition profile of transesterifying substances got flattened and saturated. Beyond which there was negligible change in content.

6.2 Experimental Validation of Theoretical Results

Experimental validation of theoretical results is shown in Figure 4. This figure shows a typical fitting of experimental results by theoretical equations (Equation 2). In most cases experimental results deviated from theoretical values within ± 20% confidence limit. This curve fitting indicates that order of reaction for DG is

2 as described in Equation (1). Reaction rate co-efficients resulting from this curve fitting are tabulated in Table 2. These rate co-efficients are unique for the transesterification reaction as described in Equation (1).

6.2 Simulation of transesterification process

After experimental validation, simulation has been done over a wide range of transesterification duration. The simulated results are presented in Figure 5. This theoretical simulation shows sigmoid curves for dynamic composition profile of TG, DG, MG and ME. These curves signify initial slow start up followed by rapid surge and finally saturated equilibrium as equilibrium is approached. Simulation results indicated that it is possible to achieve optimum RME production in 15 minutes reaction beyond which all substances get saturated and there is negligible progress in transesterification with time. Figure 6 shows simulated dynamic conversion profile of transesterifying substances. Optimum conversion is achieved in 15 minutes transesterification.

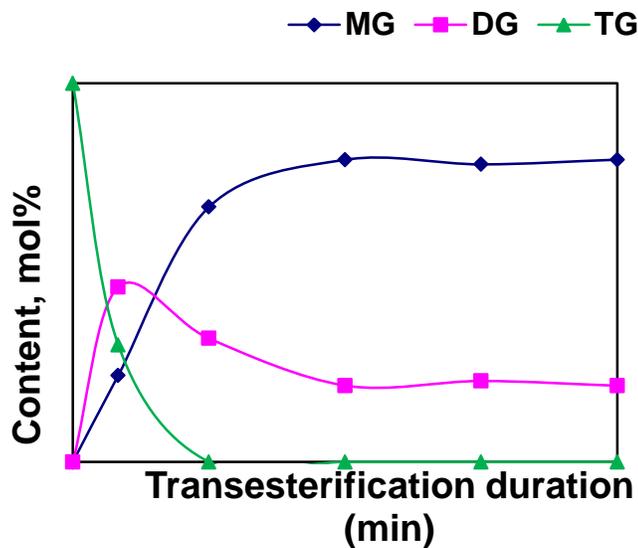


Figure 3: Dynamic Content Profile of Substances in Rapeseed Oil Transesterification

Table 1: Properties of Transesterifying Products

Transesterification duration (min)	Water content after neutralization with H ₃ PO ₄ (ppm)	pH (after H ₃ PO ₄ & water wash)	Flash point (°C)
0	-	-	-
5	274.36	5	170
15	150.64	5	165
30	251.82	5	>150
45	224.68	5	>150
60	196.80	5	>150

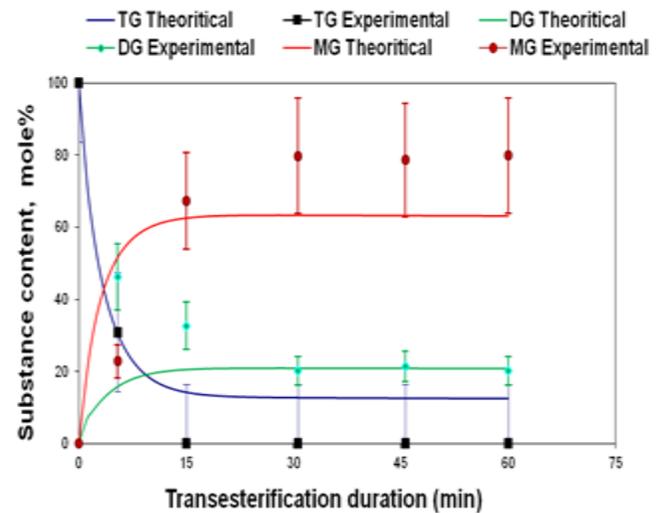


Figure 4: Dynamic composition profile of mono-, di- and triglyceride during transesterification (dots are experimental points and solid lines are theoretical prediction)

Table 2: Reaction Rate Co-efficients for Rapeseed oil Transesterification with Methanol (KOH as Catalyst)

Temperature (°C)	K values	This work	Work done by Klofutar et al., 2010 [12]
60	K1, mol ⁻¹ .min ⁻¹	0.001	
	K2, mol ⁻¹ .min ⁻¹	0.003	
	K3, mol ⁻¹ .min ⁻¹	0.009	
	K4, mol ⁻¹ .min ⁻¹	0.00003	
	K5, mol ⁻¹ .min ⁻¹	0.0213	
	K6, mol ⁻¹ .min ⁻¹	2	
	Kca, min ⁻¹	0.00708	
50	K ₁ , mol ³ .Kmol ⁻¹ .min ⁻¹		0.09
	K ₂ , m ³ .Kmol ¹ .min ⁻¹		0.5
	K ₃ , m ³ .Kmol ⁻¹ .min ⁻¹		0.156
	K ₄ , m ³ .Kmol ⁻¹ .min ⁻¹		0.1
	K ₅ , m ³ .Kmol ⁻¹ .min ⁻¹		0.7
	K ₆ , m ³ .Kmol ⁻¹ .min ⁻¹		0.0061
	Kca, mS ⁻¹		1.16×10 ⁻³

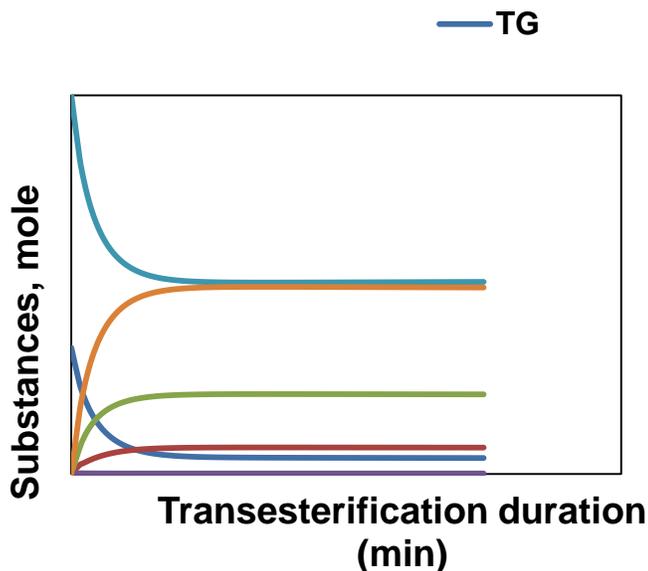


Figure 5: Simulated dynamic composition profile of substances during transesterification

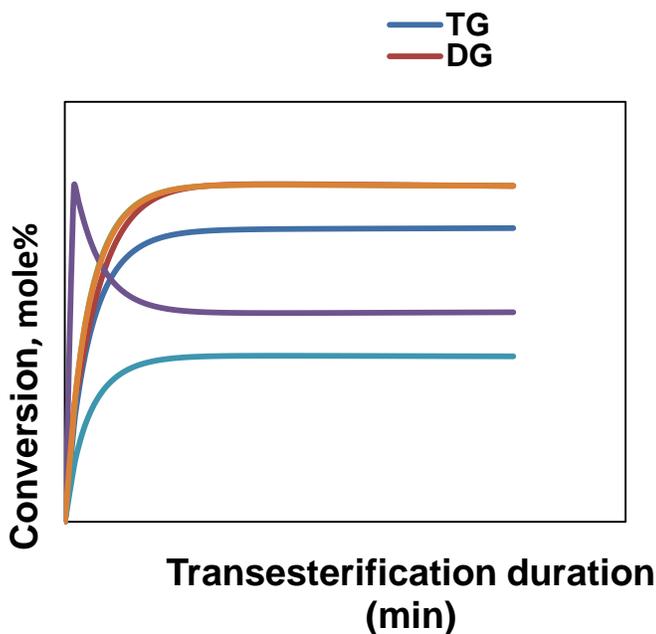


Figure 6: Simulated Dynamic Conversion Profile of Substances during Transesterification

7. CONCLUSION

Transesterification of rapeseed oil with catalyzed methanol and corresponding kinetic modeling have been accomplished in this study. Experimental results are in good agreement with the results obtained from theoretical analysis. Experimental analysis revealed sigmoid curves for transesterifying substances. Theoretical kinetic modeling predicted optimum

performance condition for this transesterification process. This kinetic modeling is also helpful to predict performance beyond experimental limit. However, this kinetic modeling is not sufficient to predict completely transesterification. Because exact order of reaction is unknown, Nevertheless, this information is essential for modeling, simulation, construction and operation of plug flow transesterification reactor which is the next step of our research.

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LIST OF SYMBOLS

Nomenclature

A	Alcohol (mol)
DG	Diglyceride (mol)
G	Glyceride (mol)
K	Reaction rate co-efficient ($\text{mol}^{-1}.\text{min}^{-1}$)
$K_{c,a}$	Mass transfer co-efficient (min^{-1})
GC	Gas Chromatograph
ME	Methyl ester (mol)
MG	Monoglyceride (mol)
N	Normality of substance (mol.L^{-1})
RME	Raps methyl ester (mol)
TG	Triglyceride (mol)
V	Volume of substance (L)
t	Time (min)
T	Temperature ($^{\circ}\text{C}$)

(Greek) symbols

d	Differential (-)
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Subscripts

I=1,2,3,4,5,6	Substances
B.Cs	Boundary conditions

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