



Research Paper

Optimization of process variables for laboratory scale production of oleochemical product sheaolein ethylester through transesterification

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ABSTRACT

Sheaolein is a fractionated product of shea butter extracted from African shea nut. Extensive herbal properties of sheaolein have made it an attractive ingredient in cosmetic industries. Sheaolein is highly viscous, semi-solid at room temperature and causes problems in oil transfer system. Transesterification of sheaolein is one of the ways of reducing its viscosity through splitting off its glycerol backbone. For this purpose, transesterification of sheaolein with ethanol in the presence of KOH catalyst was carried out in this study. Process variables: (1) reaction time, (2) catalyst concentration and (3) stirring speed were optimized to obtain better phase separation and higher yield of ethylester production. Kinetic modeling and simulation were carried out to aid process optimization. It was observed that 10-30 min reaction time, 1-1.5% KOH catalyst by weight of sheaolein oil and 500 rpm stirring speed gave better phase separation between ethylester and glycerol phases; and produced an ethylester yield of 87.92%. Production of intermediate by-products is also low at these process conditions. The results of this study will enable production of high quality oleochemical product ethylester from sheaolein in continuous industrial scale transesterification process.

Key words: Catalyst, cosmetics application, kinetics, optimization, sheaolein, ethylester, transesterification.

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Symbols: **A**, Alcohol (mol); **DG**, diglyceride (mol); **EE**, ethyl ester (mol); **G**, glyceride (mol); **H₂**, hydrogen (mol); **H₂O**, water (mol); **K**, reaction rate co-efficient (mol⁻¹.min⁻¹); **KOH**, potassium hydroxide (mol); **K_a**, mass transfer co-efficient (min⁻¹); **GC**, gas chromatograph; **MG**, monoglyceride (mol); **N**, normality of substance (mol.L⁻¹); **R**, alkyl radical (mol); **RO⁻**, alkoxide ion (mol); **ROH**, alcohol (mol); **ROK**, potassium/alkali alcoholate (mol); **TG**, triglyceride (mol); **V**, volume of substance (L); **W**, weight (g); **Wt**, weight (g); **t**, time (min); **T**, temperature (°C).

(Greek) symbols: **d**, Differential (-); **g**, gas.

Subscripts: **B.Cs**, Boundary conditions; **I**, initial; **1,2,3,4,5,6**, substances.

INTRODUCTION

Sheaolein is produced from shea butter. Shea butter is a tiny yellowish or ivory-colored fat extracted from the nut of the African shea tree (*Vitellariaparadoxa*). It is widely used in cosmetics as a moisturizer, salve or lotion. It is edible and is used in food preparation in Africa. Often the chocolate industry uses shea butter mixed with other oils, as a

substitute for cocoa butter, but the taste is different (Cidell and Alberts, 2006). Sheaolein is produced by the process of fractionating the natural shea butter to separate the olein (liquid) and the stearin (solid). Sheaolein is therefore the liquid part of the shea butter. Because of its unique herbal properties, sheaolein is extensively used in moisturizing

and heating skin ailments (Garba and Nwawe, 2011). One problem associated with the use of neat sheaolein is its relatively high viscosity of 80 mm²/s at 50°C (Olaniyan and Oje, 2007). Possible process for the reduction of viscosity is splitting off glycerol backbone thorough transesterification. Due to toxicity, methanol is not suggested for use in the transesterification of sheaolein. Relatively non-toxic, mild and similar characteristics of ethanol make it suitable for transesterification of sheaolein.

The present study focuses on the transesterification of sheaolein to reduce its viscosity, thus allowing its convective transport at room temperature. The purpose is to describe the kinetic behavior of the transesterification process of the sheaolein (vegetable oil) in order to facilitate the handling of bioester produced since it has the characteristics of low viscosity.

Reaction kinetics of bioester/alkyl ester production by transesterification in industrial scale is still under study. To solve this issue, kinetic study (that is, reaction kinetics) of transesterification has been carried out by several researchers (Susilo and Hawa, 2011; Nouredini and Zhu, 1997; Ma and Hanna, 1998). They used edible oil and animal fat as a reactant by observing reactant's concentration gradient. However, they compromised by-product formation, which is very important for biodiesel standardization compliance. In the course of transesterification, though triglyceride is consumed, but at the same time intermediate by products are formed and decayed. This may be harmful to the alkyl ester (Goosen and Vora, 2007). This is because these intermediate by-products form crystal at low temperature and block the ester transfer line (Cabral and Cahill, 2007). Intermediate by-products monoglycerides have been identified as harmful constituents to alkyl ester because of its precipitation tendency under low temperature climate condition (Yu and Gerpen, 1998). These companion authors have shown that unsaturated mono- and diglycerides are linked with an increased tendency for causing filter blockage in alkyl ester fuelled vehicles. A number of studies have been reported in published literature on factors affecting transesterification kinetics of alkyl ester. The effect of reactants composition on transesterification has been studied by measuring substances composition remaining in batch reactor (Encinar and Gonzalez, 2010). It has been reported that methanol: oil = 9:1 molar ratio in the presence of catalyst (KOH) has contributed optimum 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 kinetics (Krishnan and Dass, 2012). It has been observed that the kinetic coefficients of TG, DG and MG increase with increase in temperature from 50 to 65°C, where KOH was used as a catalyst. This co-author

used basic catalyst (KOH) but did not neutralize it to stop transesterification after desired duration. It has been shown that with increase in temperature, transesterification rate increases due to increase in transesterification kinetics. Moreover, laboratory study has shown that increasing temperature beyond 78°C decreased ethyl ester yield. This is because boiling point of ethanol is 78°C. If transesterification occurs at boiling temperature, less reactant will be available to form the desired product. Increasing temperature, as well as stirring speed up to a saturation level increased rapeseed oil-methanol mass transfer and hence transesterification efficiency (Poljanšek and Likozar, 2011). These companion authors have reported that 60°C temperature and 500 rpm stirring speed are optimum variables for rapeseed oil transesterification. Despite the fact that transesterification studies have been conducted extensively by several authors (Yihuai et al., 2012; Hossain et al., 2012; Abdelrahman and Waseem, 2014; Joshua, 2013; Kaniz et al., 2012; Antolin et al., 2002; Akaraphol et al., 2010) on a number of vegetable oils, there is still information gap between laboratory scale study and incorporation of laboratory scale information to industrial scale production. For this, the right laboratory scale experiment and empirical kinetic co-efficients from the experiment need to be retrieved. This can act as an antecedent for process variable optimization to industrial scale production. To overcome this, the present study endeavors to determine the optimum process variables: (1) reaction time, (2) catalyst concentration and (3) stirring speed for sheaolein transesterification in batch process. Subsequently, these batch process information can be integrated into flow through industrial scale reactor so that it can be operated at higher yield of ethyl ester/bioester with reduced level of by products (that is, monoglycerides).

Problem descriptions

Issues need to be addressed in process variables optimization, and kinetic studies on sheaolein transesterification are: concentration of substances remaining, kinetic co-efficient of substances and process variables (that is, temperature, catalyst concentration and stirring speed). These information are essential to fix optimum process conditions to achieve maximum sheaolein ethyl ester formation. To obtain optimized process variables, Lab scale batch experimentation need to be carried out. This is because batch process is superior to both plug flow and continuous operation (Ridlehoover and Seagrave, 1973). 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 (Kima and Elovitzb, 2007). 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 sheaolein ethyl ester (that is, cosmetics). This sheaolein ethyl ester is a derivative of postharvest product of sheaolein.

MATERIALS AND METHODS

Chemicals

Sheaolein (C18 ~ 82-93% and mostly triglyceride) was obtained from Aarhus United, Denmark. All chemicals used in the experiment, such as ethanol, 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.

ASTM D6584/EN 14105 standard solution

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.

Procedure

Sheaolein transesterification reaction in batch process was carried out according to the standard method outlined in industrial Agricultural Products Center - Publications and Information described by Ma and Hanna (1998).

According to this method, transesterification was conducted in a 100 mL beaker. About 30 g sheaolein and 9.91 g catalyzed ethanol (3.75% KOH dissolved in $\text{CH}_3\text{CH}_2\text{OH}$) of Oil: ethanol = 1:6.35 molar ratio were pre-heated to reaction temperature of 74-76°C. The reactants were then mixed and allowed to react in 5-60 minutes. After each batch of reaction, catalyst (KOH) was neutralized with equivalent amount of H_3PO_4 (according to $V_1.N_1=V_2.N_2$ 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. Thereafter, each sample vial was centrifuged for 15 min for phase separation. Upper phase sample was taken and was analyzed for mono-glyceride (MG), di-glyceride (DG), triglyceride (TG), pH and water content. Each experimental cycle was repeated twice to ensure reproducibility.

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 HACHpH 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. The column was a 15.0 m $\times$ 320 μm , and 0.1 μm J&W 1235711 high temperature capillary GC 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 and 300°C. Oven temperature started at 50°C for 1 min, increased to 180°C at a rate of 15°C/min, to 230°C at a rate of 7°C/min and finally to 370°C at a rate of 10°C/min and held at this temperature for 5 min.

Analysis was carried out using 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-tricaproxyl 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.

Experimental set up

Schematic diagram for Sheaolein transesterification is shown in Figure 1. The system is equipped with a 100 ml beaker assembly, a thermometer, a piece of parafilm paper tightly sealing the beaker and the whole system is mounted onto a heating mantle (with magnetic stirrer @ 500 rpm) controlled by thermostat. It is observed that parafilm paper is able to seal completely the reactor beaker at 74-76°C. The evaporated ethanol (at 74-76°C) is trapped and condensed on the parafilm paper and dropped back in the reactor substances. As a result, our laboratory developed simplified transesterification reactor system works in same principle as a reflux condenser. This avoids ethanol loss due to evaporation at the reaction temperature.

Crude Sheaolein and catalyzed $\text{CH}_3\text{CH}_2\text{OH}$ are mixed intimately. Homogeneous liquid-liquid interfacial mass transfer is ensured by stirring action with magnetic stirrer which is further enhanced by the application of heat.

Stirring action induced by magnetic stirrer may not be enough to completely alleviate mass transfer effects. But application of heat reduces mass transfer constraints where at elevated temperature, lower viscosity and weak liquid-liquid phase boundary enhances the reactants mass transfer. After a pre-determined transesterification duration, esterified substances were analyzed using mass measurement techniques as outlined in the materials and methods section.

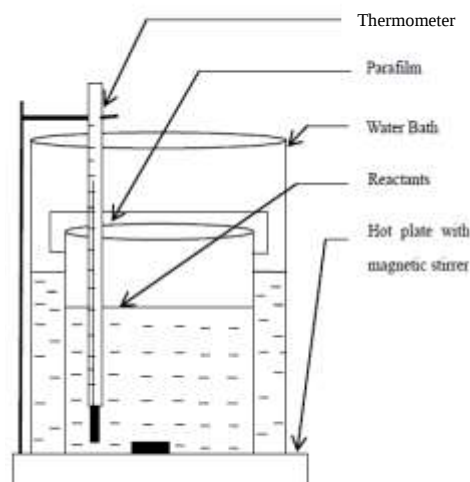


Figure 1: Schematic of setup for batch transesterification process of sheaolein.

Theoretical background

Reaction mechanism

Batch transesterification reaction mechanism of liquid (sheaolein) –liquid (catalyzed ethanol) two phase systems can be described by both mass transfer and kinetics (Poljanšek and Likozar, 2011) in terms of film model. Triglyceride from bulk glyceride phase is transferred to: (i) liquid-liquid film interface (ii) reacts at the interphase according to kinetics (transesterification reaction takes place at the bulk triglyceride–bulk alcohol interfacial film), (iii) products transfer back into bulk liquid phase. Since excess ethanol was used, the substances (the reaction mixture) have to diffuse through this phase in the reaction plane adjacent to the reaction film. Constraints are resistance associated at the interphase (mass transfer controlled and kinetic controlled) and can be characterized by concentration, mass transfer and kinetic co-efficients of initial substances (that is, triglyceride).

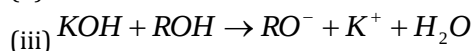
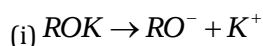
Reaction kinetics are governed by the concentration of substances and their kinetic co-efficients as shown in Figure 2(a) and (b).

According to Mittelbach and Remschmidt (2006), transesterification system between vegetable oil and alcohol is inhomogeneous with an upper alcohol phase and a lower oil phase and has to be thoroughly mixed as mentioned in experimental set up section in order to bring about reaction. In contrast to this, the ethyl esters/bioesters produced are readily miscible with alcohol. Moreover, partial glycerides and soaps are assumed to serve as emulsifiers between the starting materials. Thus the reaction mixture becomes perfectly homogeneous after a short induction period. However, once a significant amount of glycerol has been liberated, a two- phase system is established again, now consisting of

upper ester phase and a lower glycerol phase. This has been shown in our lab and industrial scale experiences. We have always found two phase system of the transesterification mixture in 0-60 min reaction where mass transfer and kinetic constraints are dominant factors affecting the transesterification.

Catalytic mechanism

Traditionally, homogeneous alkaline catalyst is widely used in commercial bioester/alkyl ester production. The alkoxide anion required for the reaction is produced by one of the following strategies (Mittelbach and Remschmidt, 2006). It can be obtained by directly dissolving an alkali alcoholate in alcohol (i), by reacting the alcohol with pure alkali metal (ii), or by adding an alkali hydroxide (iii):



Steps (i)-(iii) are production of the actual catalytic species in alkoxide-catalyzed transesterification.

Alkoxide thus produced, imparts transesterification by sequentially attacking carboxyl group of the vegetable oil and by splitting off of the glycerol backbone from the oil. This results in bioester/alkyl ester production.

Predictive theories

According to the reaction mechanism (Figure 2) and for the reaction kinetics transesterification of TG with ethanol, the

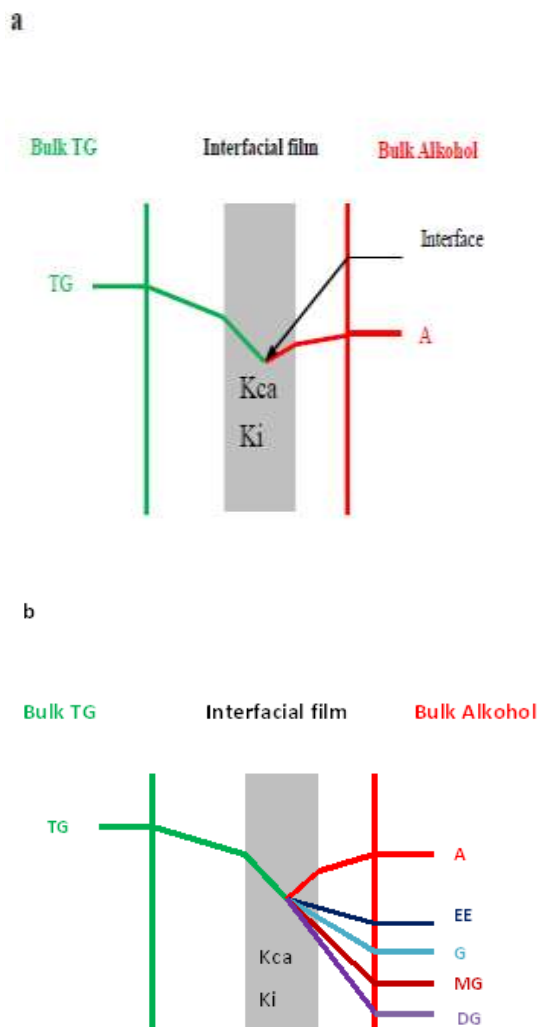
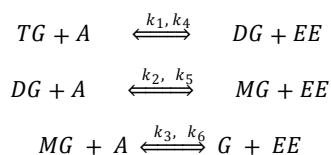


Figure 2:(a) Mass transfer coupled with reaction kinetics at liquid-liquid interface based on film model. (b) Evolution of transesterifying products. A is alcohol, TG is triglyceride, K_c is mass transfer co-efficient, K_i is reaction rate co-efficient of substance i, EE is ethyl ester, G is glyceride, MG is monoglyceride and DG is diglyceride.

presence of an alkaline catalyst give rise to esters of fatty acids (that is, ethyl ester, EE) and G. DG and MG are intermediates. The reaction steps are in Equation 1 where K_{1-6} are the 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.



.....(1)

The generic set of rate equations, taking into account mass

transfer and stepwise reactions involved in the transesterification of TG, are given in Equation 2:

$$\begin{aligned}
 \frac{d[TG]}{dt} &= k_c a ([TG]_i - [TG]) - k_1 [TG][A] + k_4 [DG][EE] \\
 \frac{d[DG]}{dt} &= k_1 [TG][A] - k_2 [DG][A] - k_4 [DG][EE] + k_5 [MG][EE] \\
 \frac{d[MG]}{dt} &= k_2 [DG][A] - k_3 [MG][A] - k_5 [MG][EE] + k_6 [G][EE] \\
 \frac{d[G]}{dt} &= k_3 [MG][A] - k_6 [G][EE] \\
 \frac{d[A]}{dt} &= -k_1 [TG][A] - k_2 [DG][A] - k_3 [MG][A] + k_4 [DG][EE] + k_5 [MG][EE] + k_6 [G][EE] \\
 \frac{d[EE]}{dt} &= k_1 [TG][A] + k_2 [DG][A] + k_3 [MG][A] - k_4 [DG][EE] - k_5 [MG][EE] - k_6 [G][EE]
 \end{aligned}$$

Numerical solution

POLYMATH 6.10 build 261 software was used to solve

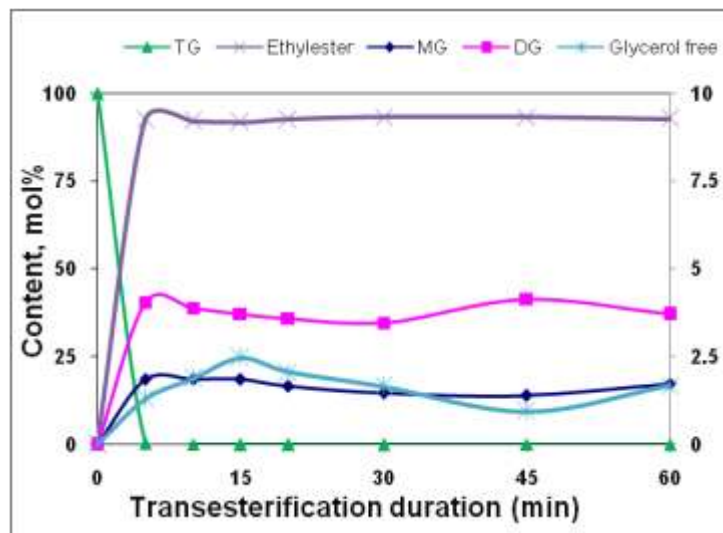


Figure 3: Dynamic composition profile of substances in sheaolein transesterification in a batch reactor (dots are experimental points and solid lines are to guide the eyes). $T = 75^{\circ}\text{C}$, oil:ethanol = 1:6.35 and 500 rpm stirring speed is used for experimental condition.

ordinary differential equations described in Equation (2). Corresponding B.Cs were set and validation was accomplished by curve fitting. The boundary conditions used to solve the differential equations are: $TG(0) = 100$, $A(0) = 300$. $TG(f)$, $DG(f)$, $MG(f)$ and $A(f)$ are the values determined from POLYMATH software for a defined kinetics. Experimental validation turns out the values of kinetic co-efficients in Equation 2. Once empirical values of kinetic co-efficients are established (unique for the system), the system is simulated for a range of operating conditions. This gives a flexible dynamic simulation for the transesterification process (Figure 3).

RESULTS AND DISCUSSION

Factors affecting transesterification

The present study focused on monitoring dynamics of transesterification process at optimized process condition, that is, $74-76^{\circ}\text{C}$ and 500 rpm (Cabral and Cahill, 2007). These are dominant factors affecting transesterification. Literature studies indicated decrease in ester yield above 78°C as explained in the introduction section.

Dynamics of transesterification

Batch process demonstrated dynamics of transesterification in 0-60 min. The dynamic composition profile of transesterifying substances is shown in Figure 3. This figure shows rapid decline of TG resulting equivalent production of EE. Sigmoid curves for the evolution of MG and DG are also shown in 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 approached 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 well shown in the Figure 3 and briefly discussed in the reaction mechanism sub-section. The property of transesterifying substances is shown in Table 1.

Effect of catalyst ratio

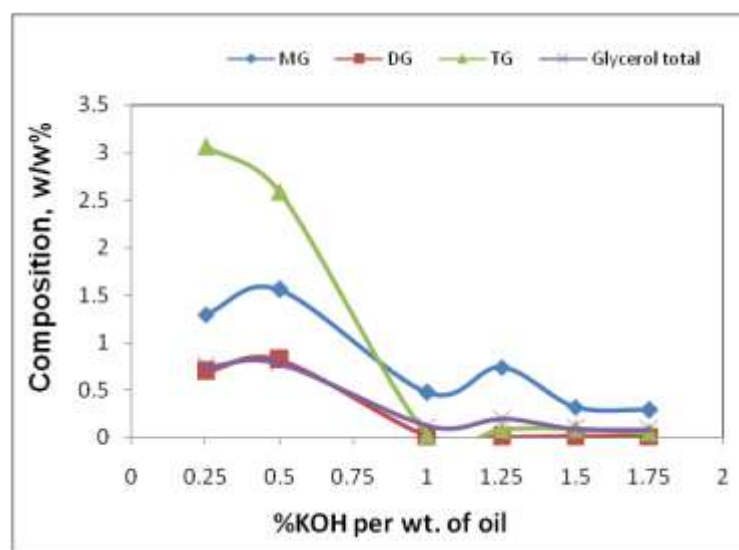
KOH was used as a catalyst in this research. Catalyst ratio has considerable impact on the transesterification of sheaolein. Composition profile of substances with a different catalyst ratio is shown in Figure 4. From this figure, it is clear that between catalyst ratios of 1-1.5, composition profile of residual substances is minimized. This means that within these catalyst ratios, equivalent ethyl ester yields are maximized. As a result, any catalyst ratio between 1-1.5 can be used for sheaolein transesterification with ethanol.

Effect of temperature

Transesterification involves reaction between two immiscible phases – sheaolein oil and ethanol phase.

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)
0	-	-
5	9,721	7.4
15	11,581	7.1
30	1,171	7.9
45	646	7.4
60	1,812	6.8

**Figure 4:** Composition profile of residual substances at different catalyst ratios in sheaolein transesterification with ethanol. T = 75°C, oil:ethanol = 1:6.35 and 500 rpm stirring speed.

Optimized transesterification temperature is reported to be 75°C (Roger and Dwight, 2000). At this temperature, the effect of phase resistances is reduced, where lower viscosity and weak liquid (sheaolein) – liquid (catalyzed ethanol) phase boundary enhanced sheaolein – ethanol mass transfer. This mass transfer is further enhanced by the application of stirring speed @ 500 rpm. As a result, faster EE conversion is achieved within this reaction temperature. As mentioned before, 78°C is the boiling temperature of one of the reactants (ethanol). So transesterification temperature should be precisely controlled to avoid this overheating because this will affect adversely yield of the transesterification.

Temperature effect implies thermodynamic limitations of the transesterification as well. Because in general, with multiple reaction, a high temperature favours the reaction of higher activation energy, and a low temperature favours the reaction of lower activation energy. As a result, kinetic effect for the overall transesterification reactions is more favorable at higher temperatures. This influence retards as the temperature is increased and the overall yield becomes

saturated at nearly the boiling point of the alcohol.

Effect of water content

Batch experiment showed that transesterification produced 646-11,581 ppm of water in 0-60 min. This water formation inhibited EE formation (Gerpen and Shanks, 2004). As a result after 15 min, the composition profile of transesterifying substances got flattened and saturated. Beyond which there was negligible change in content.

Gerpen and Shanks (2004) showed that presence of free water (>5% w/w) in the oil-alcohol system during transesterification results in hydrolysis of vegetable oil. This produces free fatty acid. The free fatty acid reacts with base catalyst (KOH) and produces soap. This results in catalyst scarcity to influence transesterification. Produced soap creates emulsion and impedes phase separation between bioster and glycerol phases. As a result, water content is an important parameter for transesterification of

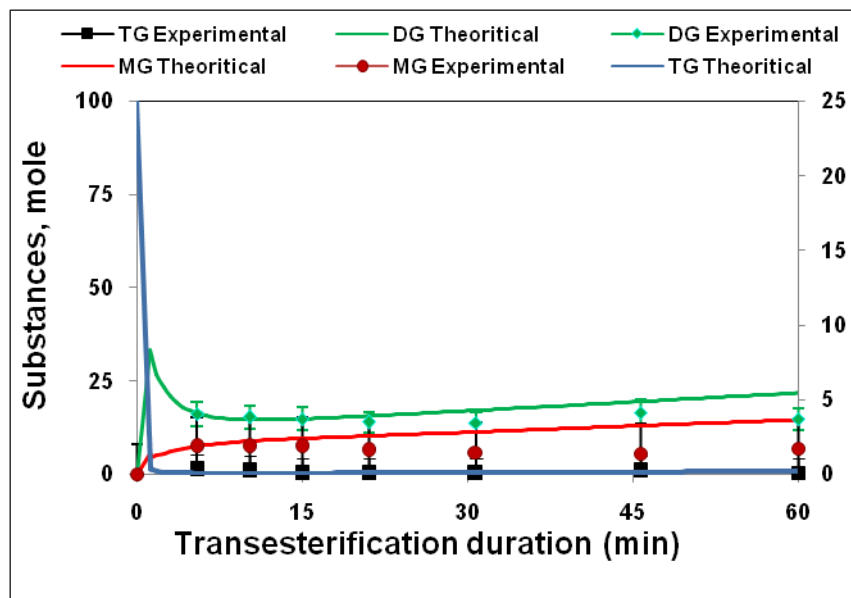


Figure 5: Dynamic composition profile of mono-, di- and tri-glyceride during transesterification (dots are experimental points and solid lines are theoretical prediction). $T = 75^{\circ}\text{C}$, oil:ethanol = 1:6.35 and 500 rpm stirring speed is used for experimental condition.

Table 2: Reaction rate co-efficients for sheaolein oil transesterification with ethanol (KOH as catalyst).

Temperature ($^{\circ}\text{C}$)	K values	This work	Work done by Klofutar and Golob (2010)
74-76	$K_1, \text{mol}^{-1}.\text{min}^{-1}$	0.07	
	$K_2, \text{mol}^{-1}.\text{min}^{-1}$	0.0035	
	$K_3, \text{mol}^{-1}.\text{min}^{-1}$	0.65	
	$K_4, \text{mol}^{-1}.\text{min}^{-1}$	0.00003	
	$K_5, \text{mol}^{-1}.\text{min}^{-1}$	0.0005	
	$K_6, \text{mol}^{-1}.\text{min}^{-1}$	0.00045	
	K_{ca}, min^{-1}	0.00708	
50	$K_1, \text{mol}^{-1}.\text{min}^{-1}$		0.082
	$K_2, \text{mol}^{-1}.\text{min}^{-1}$		0.456
	$K_3, \text{mol}^{-1}.\text{min}^{-1}$		0.142
	$K_4, \text{mol}^{-1}.\text{min}^{-1}$		0.0912
	$K_5, \text{mol}^{-1}.\text{min}^{-1}$		0.639
	$K_6, \text{mol}^{-1}.\text{min}^{-1}$		0.0056
	K_{ca}, min^{-1}		7.08×10^{-4}

vegetable oil (sheaolein).

Experimental validation of theoretical results

The experimental validation of theoretical results is shown in Figure 5. This figure shows a typical fitting of experimental results by theoretical equations (Equation 2). In most cases, experimental results deviate from theoretical values within $\pm 10\%$ confidence limit. This curve fitting indicates that order of reaction of each reactant and product

is 1 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 sheaolein transesterification reaction as described in Equation (1).

Simulation of transesterification process

After experimental validation, a dynamic simulation has been done over a wide range of transesterification

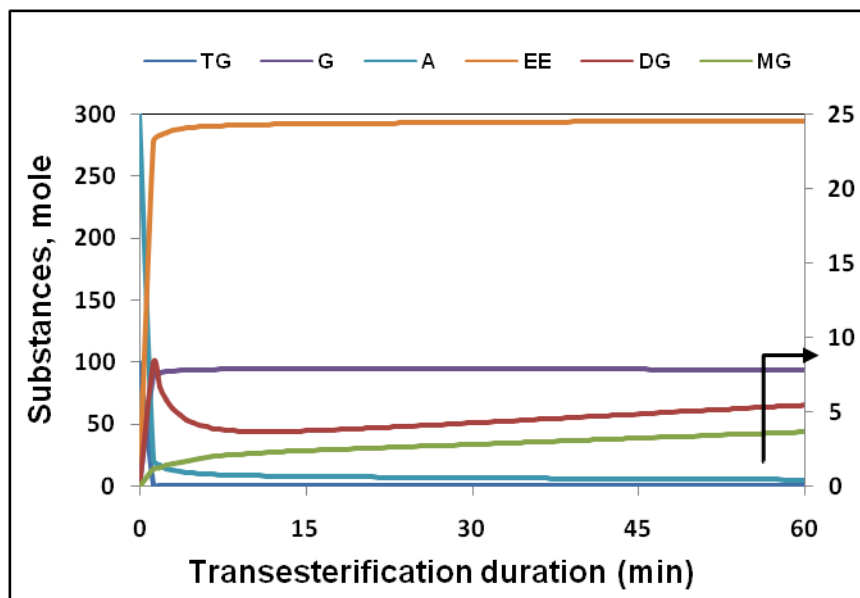


Figure 6: Simulated dynamic composition profile of substances during transesterification. TG (0) = 100 and A (0) = 300.

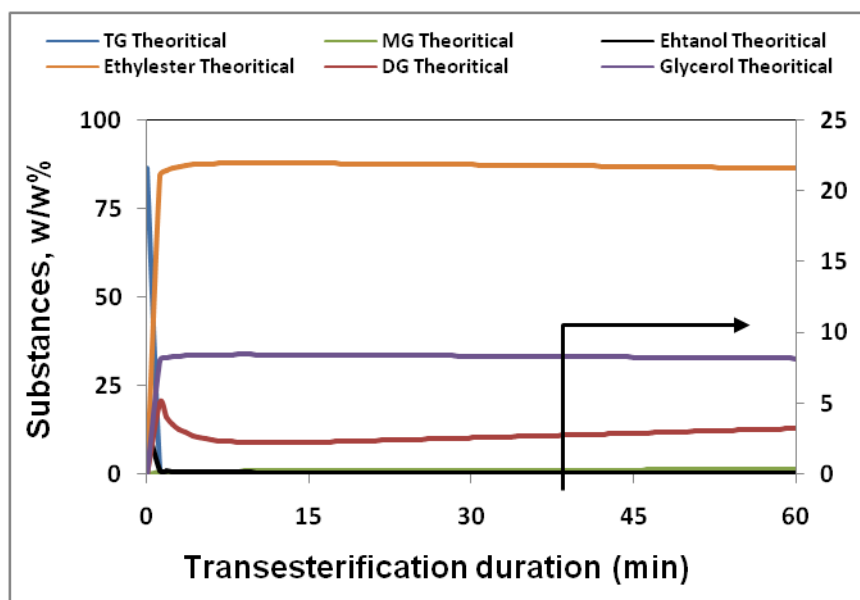


Figure 7: Simulated dynamic mass fraction of substances during transesterification. TG (0) = 87 and A (0) = 13.5.

duration. The simulated results are shown in Figure 6. This theoretical simulation shows sigmoid curves for dynamic composition profile of TG, DG, MG and EE. These curves signify initial slow startup followed by rapid surge and finally saturated profile as equilibrium is approached. Because of fast reaction, DG evolves soon after the reaction course and eventually gets saturated in about 10-11 min (3.65 mole). Multiple three step reactions favor formation of persistent intermediate by product, MG. The

persistence of MG depends on the evolution of DG and subsequent conversion of MG to EE. Theoretically, MG concentration is progressive through the transesterification duration but it becomes saturated in about 30 min (2.84 mole). Simulation results indicated that it is possible to achieve optimum EE production in 10-11 min reaction beyond which all substances get saturated and there is negligible progress in transesterification with time. **Figure 7** shows simulated dynamic mass fraction of

transesterifying substances. Optimum conversion is achieved in 10-11 min transesterification reaction.

Conclusion

Transesterification of sheaolein with ethanol as catalyst and corresponding kinetic modeling have been performed in this study. The resulting product is post-harvest derivative (sheaolein ethylester) and it is a potential ingredient of cosmetics. The experimental results are in good agreement with the results obtained from the theoretical analysis. Experimental analysis revealed sigmoid curves for transesterifying substances and optimum catalyst ratio. Theoretical kinetic modeling predicted optimum performance condition (that is, reaction time) 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 complete transesterification because the exact order of reaction is unknown. Nevertheless, the results obtained in this study are essential for modeling, simulation, construction and operation of plug flow transesterification reactor; which is the next step of our research.

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