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RESEARCH

Production of environmentally adapted lubricant basestock from jatropha curcas specie seed oil

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Abstract Jatropha curcas seed oil was studied for the synthesis of trimethylolpropane based biolube basestock via chemical transesterification of Jatropha methyl ester with trimethylolpropane (TMP) using calcium hydroxide catalyst. Reactions temperatures ranged between 80 and 160 °C and methyl esters to TMP mole ratios ranged between 3:1 and 7:1. Product analysis, ester groups and physio-chemical properties were obtained by gas chromatography, Fourier transform infrared spectroscopy and American Society for testing and material standard methods, respectively. Gibbs free energy indicated that the reaction was spontaneous with a second order rate constant of 1.00E−01 (%wt/wt min C)$^{-1}$ and kinetic energy of 13.57 kJ/mol. Jatropha biolubricant (JBL) had the following properties: viscosity of 39.45 and 8.51 cSt at 40 and 100 °C, respectively; viscosity index of 204, pour point of −12 °C and flash point of 178 °C. Temperature and mole ratio were the main factors that influenced the reaction. JBL properties complied with ISO VG 32 standard and could be applied as lube basestock with minor modifications.

Keywords Jatropha curcas · Biolubricant · Transesterification · Trimethylolpropane

Abbreviations

ASTM	American Society for testing and material
CJO	Crude jatropha oil
DE	Diesters
FAME	Fatty acid methyl ester
FTIR	Fourier transform infrared
GC	Gas chromatography
ISO	International Standard Organisation
JBL	*Jatropha* biolubricant
JME	*Jatropha* methyl ester
JTE	*Jatropha* triester
JTMPE	*Jatropha* trimethylolpropane esters
ME	Monoester
PE	Polyol ester
PUFA	Polyunsaturated fatty acid
TE	Triesters
TER	Transesterification
TMP	Trimethylolpropane
VG	Viscosity grade
VI	Viscosity index

Introduction

Strong environmental concerns and growing regulations on contamination and pollution of the environment by petroleum based lubricants have increased the need for renewable and biodegradable lubricants [1]. There have been lots of active research and development in this area due to increasing pressure from public demand, industrial concern and government agencies.

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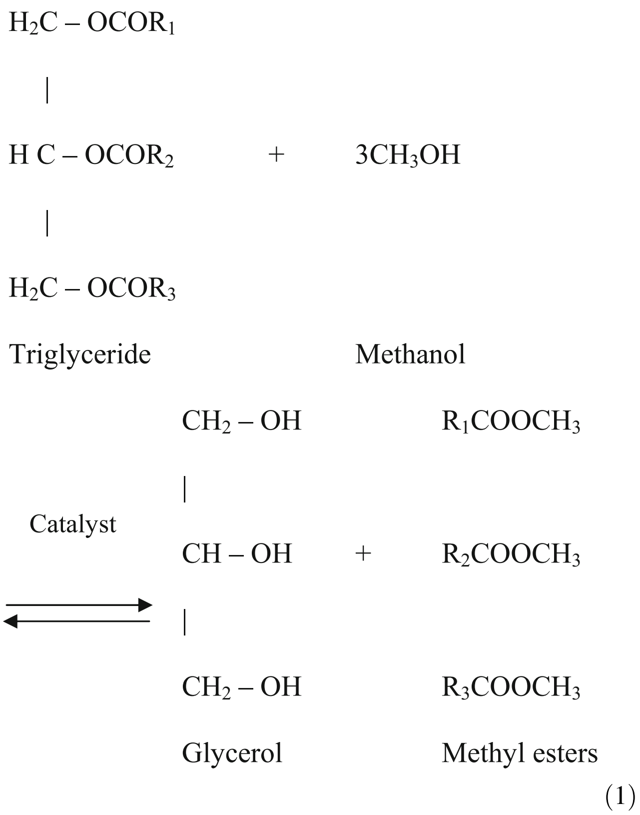
The oleochemical esters are a growing interest with respect to the base lubricants industry. Their advantages compared to mineral base oil include low toxicity, higher biodegradability, renewability, high flash point, low volatility, high additive solvency power, high added value, good lubricity (due to molecule polarity), high viscosity index due to the double bonds and molecular linearity. However, the main disadvantages of these organic compounds are oxidative instability, hydrolytic instability, low temperature properties. These disadvantages can be minimized by additives, but the biodegradability, toxicity and the price can be endangered. Thus, the chemical synthesis of these compounds seems to be a veritable choice towards eco-friendly basestocks. The additives that could be used include anti-oxidant, anti-wear, anti-corrosion, etc., which are associated with low biodegradability. However, the additives industry is working hard to develop biodegradable additives [2].

Development works reported by many studies on novel high performance biodegradable lubricants focus on reducing the market price, ecological compatibility, processes as well as technical performances [3]. Several studies focus on improving the performance of vegetable oils through modification of structures to improve their properties [4–9]. Due to its structure, unmodified vegetable oil suffers from inadequate oxidative stability, poor corrosion protection, poor hydrolytic stability and poor low temperature performance. One of the techniques that could improve the properties of the vegetable oil is to change the structure of the oil by converting it to a new type of ester called polyol ester (PE). This process eliminates the hydrogen atom on the β-carbon of the vegetable oil structure, thus providing the esters with high degree of thermal stability, seldom found in vegetable oil [10].

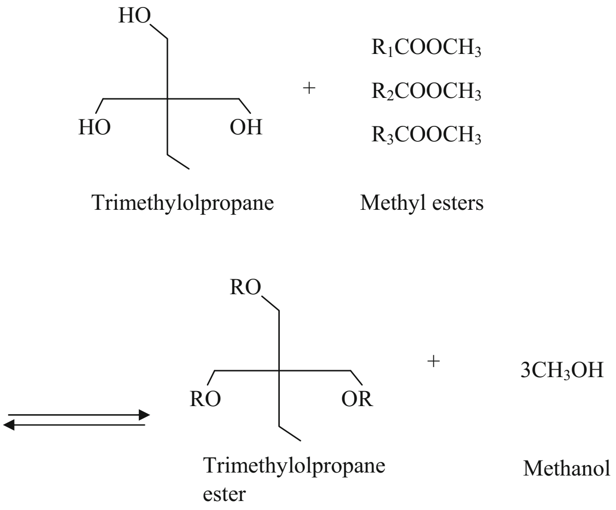
The transesterification (TER) process for biolubricant synthesis can be catalysed chemically or enzymatically. Equations (1) and (2) illustrate a two-stage base catalysed transesterification for biolubricant synthesis.

Stage one



$$\begin{array}{lcl} H_2C-OCOR_1 & & \\ \vert & & \\ HC-OCOR_2 & + & 3CH_3OH \\ \vert & & \\ H_2C-OCOR_3 & & \\ \text{Triglyceride} & & \text{Methanol} \end{array} \quad \overset{\text{Catalyst}}{\rightleftharpoons} \quad \begin{array}{lcl} CH_2-OH & & R_1COOCH_3 \\ \vert & & \\ CH-OH & + & R_2COOCH_3 \\ \vert & & \\ CH_2-OH & & R_3COOCH_3 \\ \text{Glycerol} & & \text{Methyl esters} \end{array} \qquad (1)$$

Stage two



(2)

The objective of this work is to investigate the use of Nigerian Jatropha oil as a feedstock for the production of biolubricants in a two-step base catalysed reaction of Jatropha oil methyl ester (JME) with trimethylolpropane (TMP). JME was first synthesized from crude Jatropha oil (CJO) by transesterification, after which JME was then washed and purified before used in the synthesis of Jatropha biolubricant (JBL) [11]. Process parameters that were systematically investigated include the reaction temperature, reaction time and the molar ratio of methyl ester to trimethylolpropane. Furthermore, the kinetics of the reaction was also discussed. Jatropha curcas is a shrub belonging to the family of *Euphorbiaceae*. It is a plant with many attributes, multiple uses and great potential. It is a native of tropical America, but now thrives in many parts of the tropics and sub-tropics in Africa and Asia. Jatropha curcas has the potential to become one of the world's key energy crops. At present, it is globally taking the centre stage as the oil seed of choice in biolubricant production [12–18].

The composition of Jatropha curcas oil from two different locations in Nigeria consists of main fatty acids, such as palmitic acid (14.69–14.68%), stearic acid (0–5.23%), oleic acid (0–6.06%) and linoleic acid (79.08–80.07%) [19], in addition to high percentage of unsaturated fatty acid.

This makes the oil suitable for biolubricant production because the presence of double bond will lower the melting point, which would enhance the low temperature performance of the biolubricants. Also after chemical modification, drawbacks such as instability at high temperature would be overcome thereby improving its lubricating properties.

However, the chemical compositions of the oil vary according to the climate and locality. It has been reported that there is a large variability in different accessions of Jatropha curcas from diverse agro climatic regions [20]. Accordingly, Kaushik et al [20] reported values of kinematic viscosity at 30 °C for Jatropha oil from different countries (Variety Capeverde-39cSt, Variety Nicaragua-37cSt and Variety Nigeria-17cSt). Similarly, a number of authors have carried out research works on Nigerian jatropha curcas oil from different locations across the country and obtained, to some extent, varying physicochemical properties and fatty acid composition depicted in references [19, 21–23].

Although Jatropha seed has been used as a starting material for biolubricant synthesis [20, 24–27], the process has been usually driven using conventional homogeneous catalysis. In the current study, heterogeneous catalyst was employed to drive the process. The use of heterogeneous catalyst offered the advantages of no soap production (as by-product) and easy separation of catalyst from the reaction products. In addition, in this light, inherent complementary process thermodynamics would be investigated for the consideration of the feasibility of the reaction.

Jatropha oil is non-edible due to the presence of anti-nutritional substances such as phorbol esters [24] and thus makes it suitable as biodiesel and biolubricant feedstock [25]. In Nigeria, Jatropha can grow very well and already abundant in the country, but mainly for border demarcation of farm lands [28]. It is widely cultivated in the tropics as a live fence (hedge) around farm lands, since the toxins in the plant deter animals [29]. The tree has a life span of up to 30–40 years and could grow on a wide range of land types, including non-arable, marginal and waste lands, and need not compete with vital food crops for agricultural land. Crude Jatropha oil is not edible and its price may not be distorted by competing food uses [28]. The oil content of the seed ranges between 50 and 60% [30–33].

Materials and methods

Materials

Jatropha curcas samples were collected from Idah, Kogi State, Nigeria. The seeds were cleaned, shelled and air-dried in the shade for few days. All the chemicals and reagents used for this work were of analytical grade.

Extraction of oil from jatropha seed sample

Shelled and air-dried Jatropha seeds were crushed and tied in a white piece of cloth. This was later soaked in hexane in a tightly sealed bucket for 3 days, before collecting the extract through filtration. The cloth containing the crushed Jatropha seeds was further rinsed with fresh hexane to extract more oil. The hexane contained in the extracted Jatropha oil was removed by distillation while the crude oil extract was collected in a beaker [34].

Synthesis of jatropha methyl ester

Jatropha oil extracted from Jatropha seed was transesterified to form Jatropha Methyl Ester (JME). In this method, a mixture of 300 g of Jatropha oil, 100 g methanol and 1% wt/wt orthophosphoric acid catalyst were poured into continuously stirred reactor equipped with a water-cooled reflux condenser and heated up to 65 °C for 90 min. The mixture was dosed with 0.2 molar solution of sodium trioxocarbonate IV, which on neutralizing the acid catalyst, stopped the reaction. The neutralized mixture was later transferred to a separating funnel and subsequently allowed to stand overnight to ensure complete separation of methyl esters and glycerol phases. Glycerol phase (bottom phase) was emptied into a clean container and then allowed to stand. The obtained JME was heated at 65 °C to remove methanol. Entrained catalyst in the JME was removed by successive rinses with hot distilled water. Finally, water present in the JME was eliminated by oven-heating at 70 °C [34].

Synthesis of jatropha biolubricant

This was as described by Surapoj et al. [35] with modifications. A process flow for the synthesis is shown in Fig. 1.

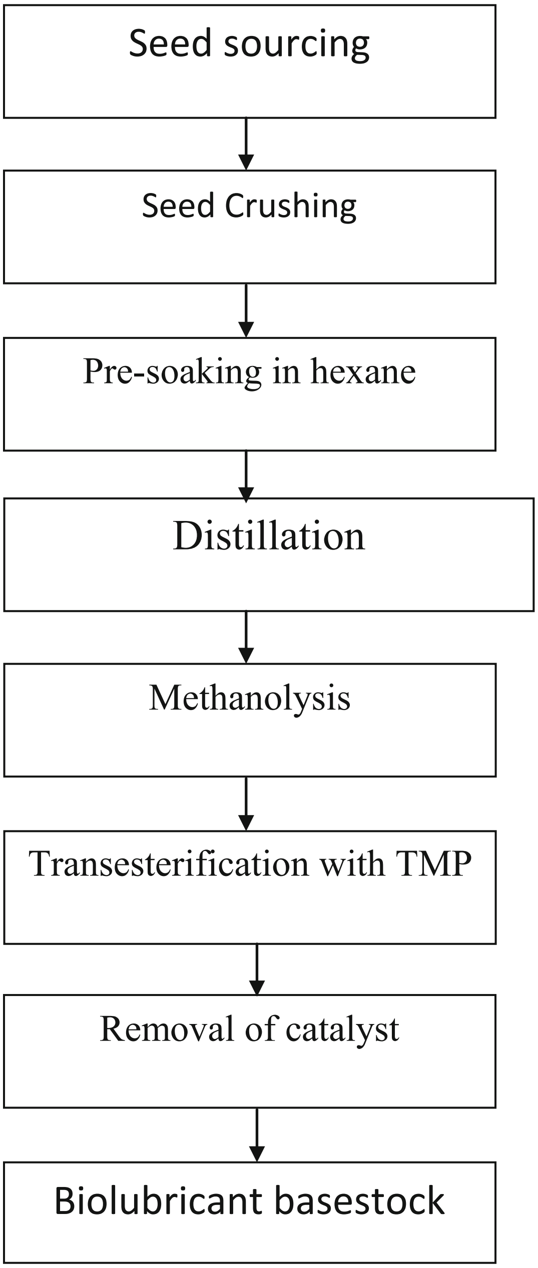


Fig. 1 Flow sheet process for biolubricant synthesis

In this method, TMP was initially heated using a transesterification experimental set-up comprising 50-mL three-necked round-bottom flask equipped with a water-cooled reflux condenser, a thermometer, Kipp's apparatus and a thermofisher scientific 50094711(THERMO SCIENTIFIC CIMAREC I MONO DIRECT) stirrer operated at 1000 rpm. The TMP contained in the flask was heated to and kept at 110 °C for 15 min, while being stirred at 1000 rpm under CO_2 flow. 110 °C was maintained to evolve moisture from the TMP. Using the same experimental set-up, a $Ca(OH)_2$ catalysed batch transesterification reactions between JME (FAME) and already cooled TMP were conducted at the following JME–TMP ratios: 3:1, 4:1, 5:1, 6:1 and 7:1. Each of the stated JME–TMP ratios was subjected to transesterification at individual temperatures of 80, 100, 120, 140 and 160 °C. Each of the individual experimental runs at a given particular ratio and temperature was monitored and samples were collected at reaction times intervals of 1, 2, 3, 4 and 5 h for analyses. At the end of each reaction, the product mixture was brought to room temperature and filtered to separate the solid catalyst from the liquid mixture (JBL). The filtered Jatropha bio-based stock was analysed using the GC to determine the product composition. Pour point, viscosities, flash point and viscosity index were also determined by appropriate analysis [34]. The unreacted methyl ester was not removed before measuring the properties of the biobased TMP ester to eliminate potential conjugation reaction at destructive high temperature (180–200 °C) molecular distillation (needed to remove unreacted methyl ester) involving poly unsaturated fatty acid (PUFA) and also improve wear resistance of the biobased TMP ester [6, 36]. Meanwhile, specified measurements of product (JBL) properties were selectively done for only JME–TMP mole ratio of 4:1 at 140 °C as indicated in "Lubricating properties of jatropha biolubricant".

Analysis of transesterification product

Functional groups present in JBL were identified through Fourier transform infrared resonance (FTIR). Samples were collected at hourly reaction times intervals (for a total period of 5 h) and analysed for JME, monoester (ME), diesters (DE), triesters (TE) and TMP by gas chromatography. The yield of each product was determined from the GC chromatogram calibrated against the known samples according to the procedure described by Yunus et al. [37].

Lubricating characteristics

The following named lubricating characteristics were determined based on the corresponding referred American Society for testing and material (ASTM) procedures: Pour

Point [38]; Kinematics Viscosities [39]; Viscosity Index [40] and Flash Point [41].

Results and discussion

Fourier transform infrared (FTIR) analysis of the JBL

The FTIR analysis (Fig. 2) was performed to determine the functional groups present in the biolubricant. Sample's discernable peaks ranged between 4000 and 700 cm^{-1}. The peaks located at 1228.3599 and 1171.4302 cm^{-1} corresponding to C–O stretching, indicated the presence of esters. The band at 1737.808 cm^{-1} was for C=O stretching, usually present in the esters. The peak at 2890.222 cm^{-1} (C–H stretching and CH_2 stretching) indicated the presence of carbohydrate and nucleic acids. The peak at 1737.808 cm^{-1} (C=O stretching) showed the presence of fats. For O–H stretching and phenol O–H stretching characterized by 3463.213 cm^{-1}, the presence of water and phenols were indicated [33, 42].

Time lined transesterification of TMP with JME

Figures 3 and 4 and S1–S3 indicate the progress of transesterification reactions at different times. It was observed that transesterification proceeded stepwise, in which ME formation first reached a maximum value. This was followed by a steady formation of DE. At the point of

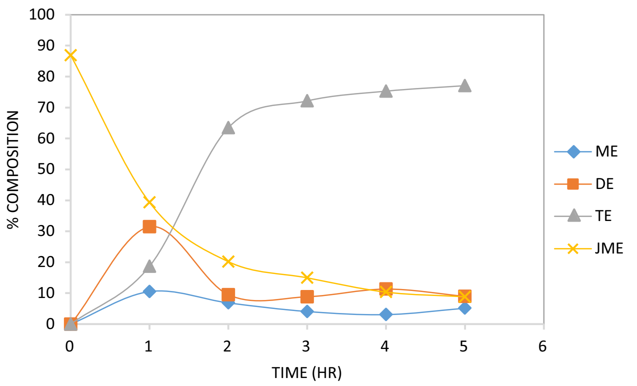


Fig. 3 TER between TMP and JME of 140 °C and 3:1 molar ratio using 1 wt% $Ca(OH)_2$ catalyst

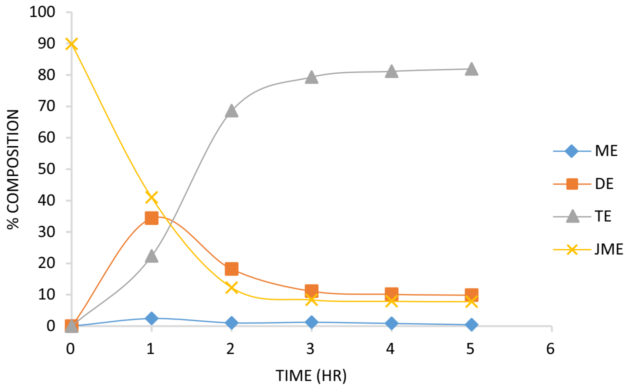


Fig. 4 TER between TMP and JME of 140 °C and 4:1 molar ratio using 1 wt% $Ca(OH)_2$ catalyst

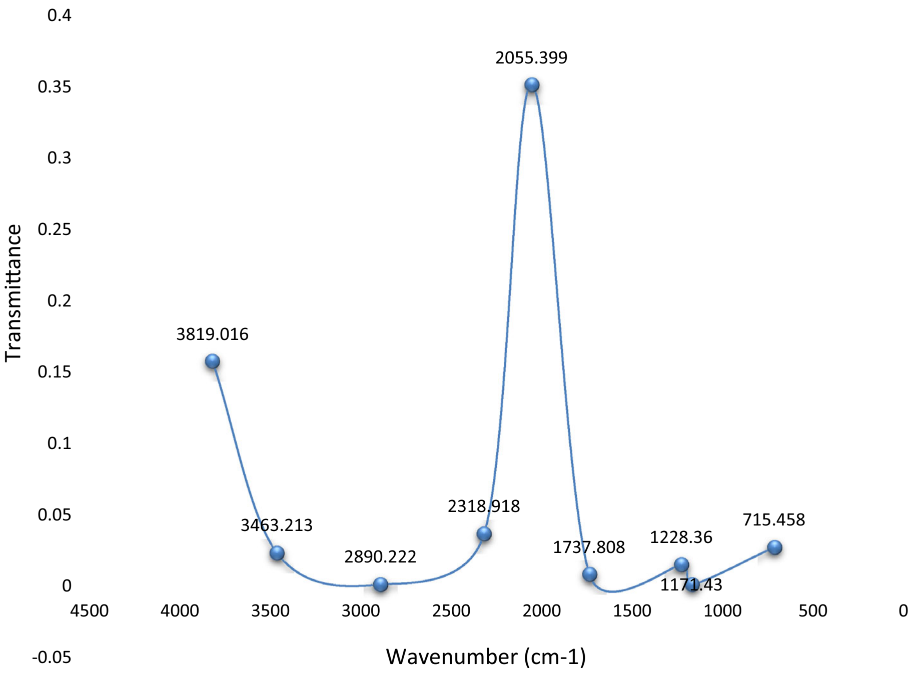


Fig. 2 FTIR spectrum of Jatropha TMP ester

maximum formation of DE, TE increased rapidly. This was because the transesterification stepwise process preceded with the formation of intermediates products, before the commencement of the formation of final desired product, which was the TE [37]. Initially, ME, which was a single branch polyol ester was formed during the reaction. The increasing amount of ME, however, would immediately undergo conversion to form DE, which would react with JME to produce TE. Concentration of TE would rise with the decrease of DE and ME concentrations. Similar reaction mechanism has been reported earlier by other researchers [34, 43, 44].

Effects of temperature

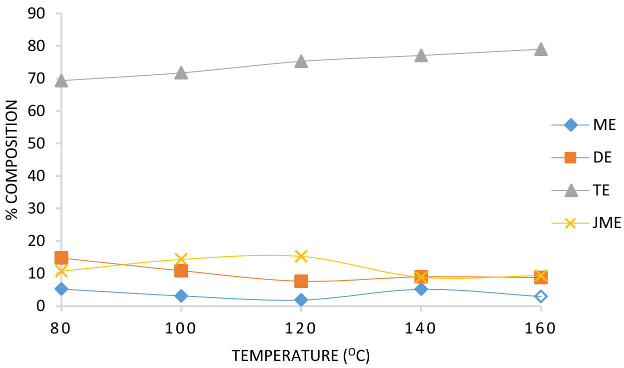


Fig. 5 Effects of temperature on JTMPE composition at 3:1 JME–TMP mole ratio and 1% catalyst loading for 5 h

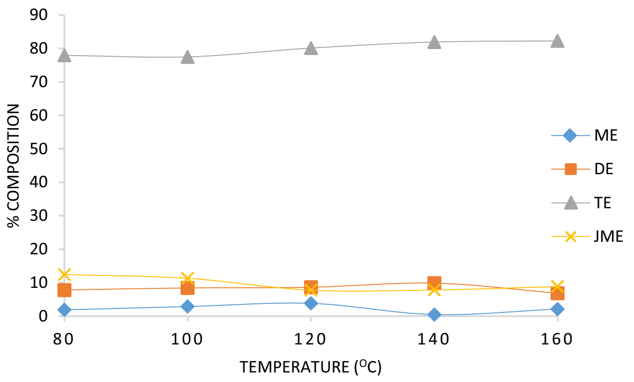


Fig. 6 Effects of temperature on JTMPE composition at 4:1 JME–TMP mole ratio and 1% catalyst loading for 5 h

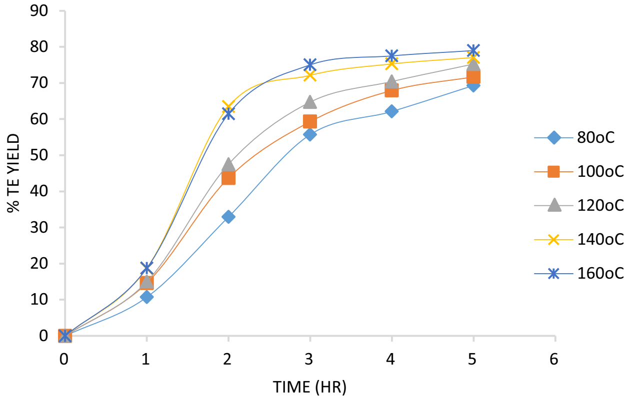


Fig. 7 Temporal yield of JTE at various temperatures, 3:1 JME–TMP mole ratio and 1% catalyst loading

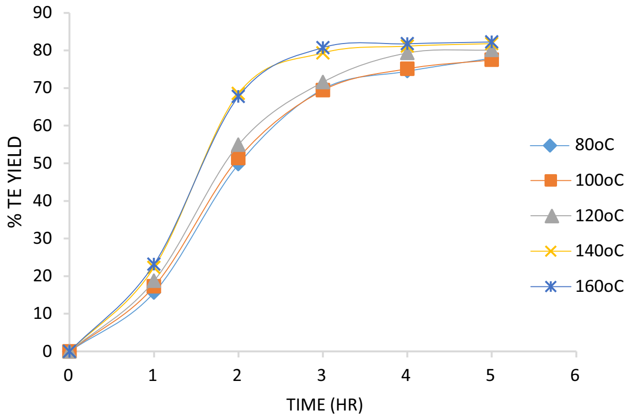


Fig. 8 Temporal yield of JTE at various temperatures, 4:1 JME–TMP mole ratio and 1% catalyst loading

To determine the effect of temperature, a series of experiments was conducted at JME–TMP molar ratios of 3:1, 4:1, 5:1, 6:1 and 7:1. Catalyst (Ca(OH)$_2$) amount was fixed at 1.0% wt/wt of reaction mixture. The reactions monitored for 1–5 h were carried out at 80, 100, 120, 140 and 160 °C for each of the mole ratio to observe the effect of temperature on the transesterification products. Representative results of the syntheses are shown in (Figs. 5, 6 and S4–S6) and (Figs. 6, 7 and S7–S9). Figures 4 and 5 and S4–S6 show the influence of temperature on the production profile of Jatropha trimethylolpropane esters (JTMPE or JBL) consisting of mono ester (ME), diester (DE), trimester(TE) and unreacted JME. Figures 5 and 6 and S4–S6 indicated that as the temperature increased, the TE composition increased, until at about 140 °C, after which the increase in TE composition became marginal. This was because at higher temperature, the amount of FAME in the reactor was low as a result of vaporization, enhancing the occurrence of the reverse reaction. By re-condensing the FAME (i.e. JME in this study) vapour back into the reactor, the reverse reaction would be contained and the esterification of DE to TE would prevail. Hence, water used in the condenser should be cold enough to ensure condensation of the vaporized FAME back to the reactor [34, 45, 46]. The amount of ME, DE and JME, would be considered insignificantly unchanged with temperature variation. Figures 7 and 8 and S7–S9 depict the influence of temperature specifically on temporal yield profile of Jatropha triester (JTE), which was the major active ingredient in JBL.

Figures 7 and 8 and S7–S9 indicated that generically, the yield increased with increase in time for all the temperatures considered. Expectedly, least yield was obtained at 100, since least successful molecular collision for product formation would be the case.

Effects of mole ratio

Transesterification, being a reversible reaction, could be driven to enhance the yield of triesters using excess amount of FAME or TMP. Excess FAME was chosen over TMP due to its relative lower cost. The same pattern of experiments as described in "Effects of temperature" applied here for the study of influence of mole ratio on the % composition of transesterification products. Figures 9 and 10 and S10–S12 represent the results of the effect of mole ratio on % composition of JTMPE at 120 and 140 °C, respectively. On the other hand, Figs. 11 and 12 and S13–S15 represent the results of the temporal yield of JTE at various mole ratios for temperatures of 120 and 140 °C, respectively. Figures 9 and 10 and S10–S12 indicate that when molar ratio of FAME: TMP was increased, TE yield increased. Generally, a better product yield was obtained by keeping the molar ratio of reactants higher than the stoichiometric values since the reaction was driven more towards completion. This is in consonance with Le Chatelier's principle. According to Le Chatelier's principle, an excess of TMP would increase the TE yield by shifting the equilibrium to the right. However, excess JME was used in this study due to its relatively lower cost compared to TMP. However, from Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 and S13–S15, it was obvious that increasing the molar ratio above 4:1 provided marginal gain in TE yield. This could be due to onset of reverse reaction that retarded the conversion of DE to TE [38]. In the chemical and enzymatic transesterification of rapeseed methyl ester with TMP, maximum conversion was obtained at 3.3:1 and 3.5:1, respectively [44]. Yunus et al. [37] reported optimal transesterification process at palm oil methyl ester (POME)—TMP ratio of 3.8:1, 120 °C, 0.9% sodium methoxide catalyst and 20 Mbar [44]. In the report [37], conversion to TE increased from 83 to 86% as the ratio was increased from 3.5:1 to 3.7:1 [34]. Table 1 shows TE yield at various combinations of temperature and JME–TMP mole ratios.

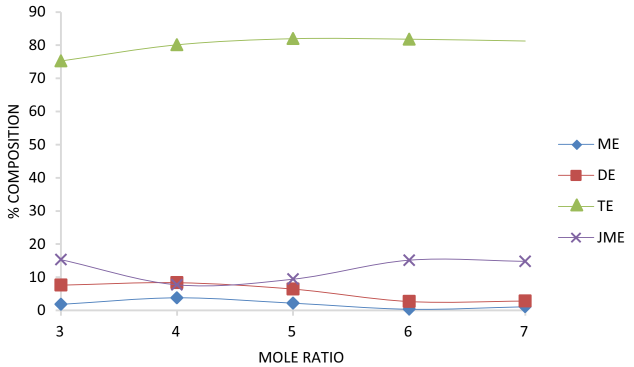


Fig. 9 Effects of JME:TMP mole ratio on % composition of JTMPE at 120 °C and 1% catalyst loading

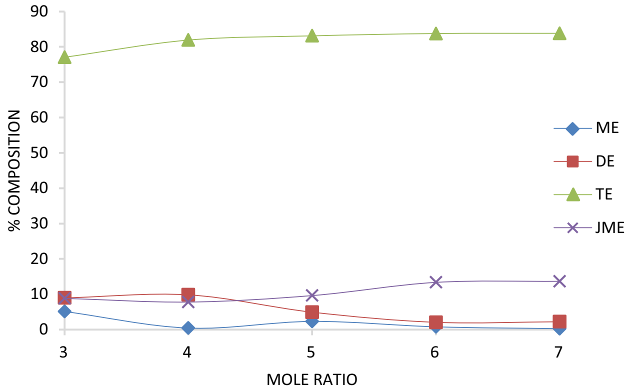


Fig. 10 Effects of JME:TMP mole ratio on % composition of JTMPE 140 °C and 1% catalyst loading

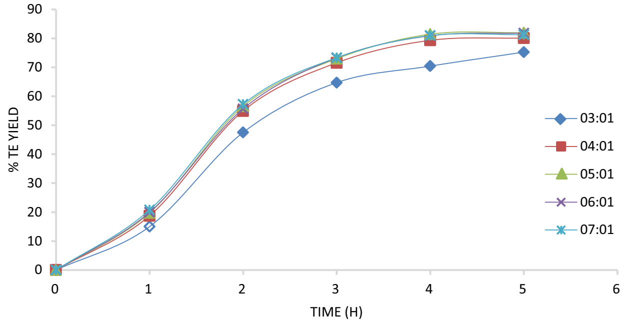


Fig. 11 Temporal yield of JTE at various mole ratios, 120 °C and 1% catalyst loading

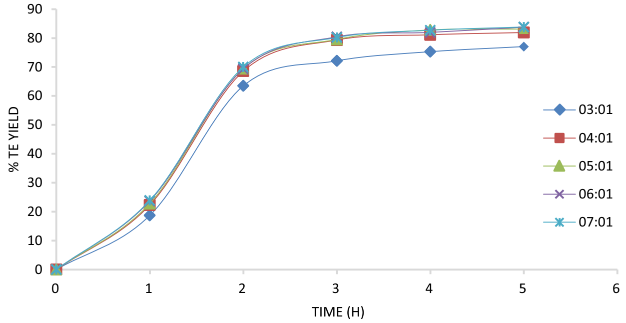


Fig. 12 Temporal yield of JTE at various mole ratios, 140 °C and 1% catalyst loading

Table 1 Percentage TE yield at various combinations of temperature and JME–TMP mole ratio

Temp (°C)	Mole ratio				
	03:01	04:01	05:01	06:01	07:01
80	69.71	77.93	77.87	79.32	80.25
100	71.71	77.48	77.59	77.97	76.79
120	75.25	80.12	81.97	81.82	81.27
140	77.06	81.92	83.11	83.77	83.83
160	78.98	82.26	82.94	83.64	84.12

Kinetics of transesterification of FAME and TMP

Transesterification reaction is a consecutive and reversible reaction being driven by excess FAME and a catalyst. The reaction could be represented as follows [26, 34]:

$$\mathrm{FAME} + \mathrm{TMP} \leftrightarrow \mathrm{ME} + M \tag{3}$$

$$\mathrm{FAME} + \mathrm{ME} \leftrightarrow \mathrm{DE} + M \tag{4}$$

$$\mathrm{FAME} + \mathrm{DE} \leftrightarrow \mathrm{TE} + M \tag{5}$$

Overall reaction:

$$3\mathrm{FAME} + \mathrm{TMP} \leftrightarrow \mathrm{TE} + 3M \tag{6}$$

Kinetics study was conducted to determine the reaction order and rate constants for the reaction time ranging from 1 to 50 min. The best JME:TMP ratio of 4:1 obtained from the batch transesterification study was used for the kinetic study while considering TMP as the limiting reactant. Figures 13 and 14 show the kinetics plots for the transesterification process at various temperatures for the first 50 min.

The best kinetic model for the data appears to be a second order kinetics. A model was developed based on the kinetics of decreased concentration of trimethylolpropane [26, 34]. The second order reaction rate law for this study would be as follows:

$$\frac{1}{\mathrm{TMP}} = K_{\mathrm{TMP}}t + \frac{1}{\mathrm{TMP}_0} \tag{7}$$

where K_{TMP} is the overall second order rate constant, t is the reaction time, TMP_0 is the initial trimethylolpropane concentration, TMP is final concentration of trimethylolpropane.

For transesterification reaction, a plot of reaction time versus 1/[TMP] will be straight line if the model would be valid. The rate constants for different temperatures were calculated from the slope and presented in Table 2, together with the corresponding R^2 values for both first and second order kinetics.

The first-order kinetic equation can be expressed as:

$$\ln([\mathrm{TMP}_0/\mathrm{TMP}]) = Kt \tag{8}$$

There was an increase in k at higher temperature. This indicated an increase in the reaction rate as the temperature increased for the temperature range studied. Table 3 summarizes the overall rate for both the first and second order kinetics at different temperatures.

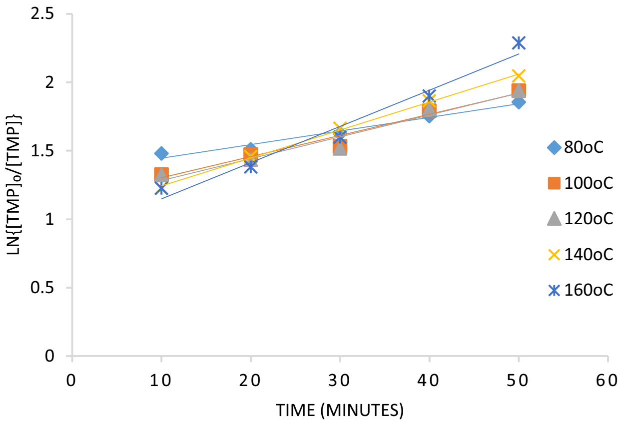


Fig. 13 First order kinetics plot for the synthesis of JBL at various temperatures (4:1 JME–TMP mole ratio)

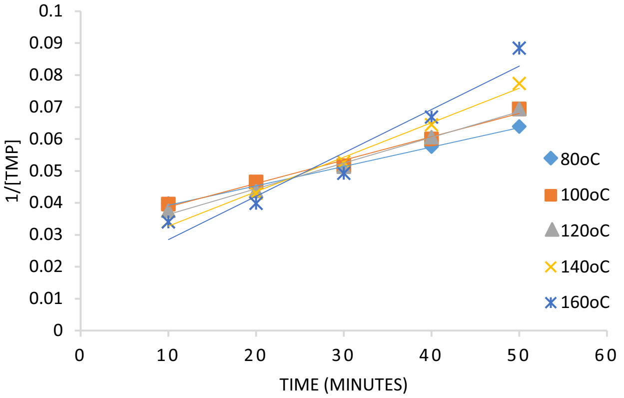


Fig. 14 Second order kinetics plot for the synthesis of JBL at various temperatures (4:1 JME–TMP mole ratio)

Table 2 Rate constant, K_{TMP} and regression values at various temperatures (JBL)

Temperature (°C)	First order		Second order	
	$K_{\mathrm{TMP,1st}}$ (%wt/wt min)	R^2	$k_{\mathrm{TMP,2nd}}$ (%wt/wt min)$^{-1}$	R^2
80	9.90E−03	0.9697	6.00E−04	0.9977
100	1.55E−02	0.9674	7.00E−04	0.988
120	1.60E−02	0.9596	8.00E−04	0.9941
140	2.04E−02	0.9983	1.10E−03	0.9938
160	2.64E−02	0.9703	1.40E−03	0.9419

Table 3 Comparison between the overall first and second order kinetics with temperature dependence

Rate of reaction	Overall 1st order		Overall 2nd order	
	(%wt/wt min °C)	R^2	(%wt/wt min °C)$^{-1}$	R^2
k_{TMP}	1.895E−02	0.9479	1.00E−01	0.9469

Activation energy

The activation energy of the transesterification reaction was determined based on the well-known Arrhenius Eq. (9):

$$\log_{10^k} = (-E^{\pm}/2.303RT) + \log_{10} A \tag{9}$$

where R is the gas constant (kJ/molK), T is temperature in Kelvin. The logarithm of the reaction rate data was plotted as a function of reciprocal of temperature and the activation energy was calculated from the slope of the regression line and presented in Table 4. Activation energy may be defined as the minimum energy required for starting a chemical reaction. The activation energy for JBL synthesis was 13.57 kJ/mol. Mohammad et al. have reported activation energy of 1.65 kJ/mol for Jatropha biolubricant synthesis [26]. The differences in the activation energies could be due to disparities in the reaction temperatures.

A high temperature is needed for high activation energy reaction while low temperature is needed for low activation energy reaction. In kinetic analysis, often times when low activation energy is accompanied with high temperature, it results in high rate constant and hence speeding up the reaction [47]. However, both are within the same range of sensitivity toward temperature [47].

Transesterification thermodynamics

Thermodynamic parameters were systematically determined. The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction to occur. A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs, while a positive value indicates that it will not. The enthalpy (ΔH) is a measure of the actual energy that is liberated or taken when the reaction occurs. If it is negative, then the reaction gives off energy (exothermic), while if it is positive the reaction requires energy (endothermic). The entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

Table 4 Activation energy for the synthesis of jatropha biolubricants (JBL)

JBL (this work)		JBL [26]	
E (kJ/mol)	R^2	E (kJ/mol)	R^2
13.57	0.986	1.65	0.861

Table 5 Thermodynamic parameters for JBL synthesis

T (K)	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)
353	−30.63	−23.94	13.52
373	−31.89		
393	−33.16		
413	−33.75		
433	−34.52		

The thermodynamic properties such as free energy (ΔG), enthalpy change (ΔH) and entropy change were determined by applying the second order reaction constant K $\{(\%\text{wt/wt min})^{-1}\}$ in the Van 't Hoff Eq. (11) [34]:

$$\Delta G^{\mathrm{o}} = -RT \ln k \tag{10}$$

$$\ln k = \frac{\Delta S^{\mathrm{o}}}{R} - \frac{\Delta H^{\mathrm{o}}}{RT} \tag{11}$$

$\ln k$ was plotted against $1/T$ to determine the enthalpy change, ΔH and entropy change, ΔS as presented in Table 5. The positive value of ΔH in Table 5 indicates an endothermic reaction. The negative value for the Gibbs free energy confirmed the feasibility of the process and that the degree of spontaneity increased with increased temperatures as ΔG^{o} became more negative. The increasing negative value of ΔG^{o} with an increase in temperature indicated that the transesterification reaction became more favourable at higher temperatures. The negative ΔS value means the disorder of the system decreases [34].

Lubricating properties of jatropha biolubricant

The basic functions of a lubricant are friction and wear reduction, heat removal and contaminant suspension. Apart from important application in internal combustion engines, vehicles and industrial gear boxes, compressors, turbines or hydraulic systems, there are vast numbers of other applications, which mostly require specifically tailored lubricants. The physicochemical and performance requirements define a lubricant identity and its ability to perform these functions. The basic properties of JBL are shown in Table 6.

Table 6 Properties of JBL (at 140 °C, 4:1 JME–TMP mole ratio)

Property	Units	JBL	CJO	Method
KV @ 40 °C	cSt	39.45	17.15	ASTM D 445
KV @ 100 °C	cSt	8.51	4.83	ASTM D 445
Viscosity Index (VI)	–	204	233	ASTM D 2270
Pour Point (PP)	°C	−12	−7	ASTM D 97
Flash Point	°C	178	92	ASTM D 93

The most important property of a lubricant is the viscosity. Loosely defined, the viscosity is the fluid's ability to resist motion. Kinematic viscosities (KV) for lubricant are usually determined at 40 and 100 °C. JBL was found to have kinematic viscosities of 39.45 and 8.51 cSt at 40 and 100 °C, respectively. In an earlier work KV of 35.55 and 7.66 cSt were reported at 40 and 100 °C, respectively, for sesame oil based trimethylolpropane ester [34]. Similarly, 35.43 and 7.93 cSt KV were reported for Sesame oil TMP ester [48]. Other researchers have reported the following kinematic viscosities at 40 °C: 39.7–54.1 cSt for TMP esters of palm and palm kernel oils [6], 43.9 cSt for TMP esters of Jatropha curcas oil [26] and 11.2–36.1 cSt for TMP esters of 10-undecenoic acid [49]. They also reported the following kinematic viscosities at 100 °C: 7.7–9.8 cSt [6], 8.7 cSt [11] and 3.2–7.3 cSt [49]. These reports show a good comparison between JBL and other seed oil based lubricant.

An ideal lubricant for most purposes is one that maintains a constant viscosity throughout temperature changes. Variation in the viscosity with change in temperature of a lubricant is determined by viscosity index (VI). The importance of the VI can be shown easily by considering automotive lubricants. Oil having a high VI resists excessive thickening when the engine is cold, and consequently, promotes rapid starting and prompt circulation. It resists excessive thinning when the motor is hot and thus provides full lubrication and prevents excessive oil consumption. A very high VI is a desirable property of lubricant due to its ability to resist oxidation and thermal exposure [50]. The VI of an oil may be determined if its viscosity at any two temperatures is known. The viscosity index of JBL shown in Table 6 was found to be 204 using the kinematic viscosity values at 40 and 100 °C. Sripada [44] reported VI of 193 and 204 for the synthesis of biolubricant from methyl oleate and canola biodiesel, respectively. Similarly, Gryglewicz et al. [51] recorded high VI range of 209–235 for the synthesis of neopentyl glycol and trimethylolpropane esters of olive oil, rapeseed oil and lard fatty acids. Yunus et al. [6] found that TMP esters of palm and palm kernel oils exhibited very high VI of 167–187. According to Ghazi et al. [11] and Rao et al. [49], VI of 180 for Jatropha curcas-derived TMP esters and 162–172 for polyol esters of 10-undecenoic acid were obtained. Furthermore, Åkerman et al. [52] reported that TMP esters of C_5–C_{18} fatty acids had VI of 80–208. When compared with previous results, JBL had shown a relatively favourable VI.

Climatic conditions are important consideration when selecting lubricants. Therefore, viscosities and pour point values are important parameters needed to assess the performance of lubricants [50]. Oil thickens as the temperature falls. At a certain temperature, it no longer flows by its own weight. This temperature is called the pour point. The pour point depends on, e.g. the viscosity and chemical structure of the oil. Oil extracted from Jatropha seed was tested for pour point and viscosity and further compared with JBL. While that of crude Jatropha oil (CJO) was −7 °C, the pour point of JBL was −12 °C, indicating an improvement in pour point as a result of the transesterification reaction. This was due to the presence of polyol group in the TMP and the absence of beta-hydrogen in the final product [8, 53].

Flash point measures the readiness of the oil to ignite momentarily in air and is a consideration for the fire hazard of the oil. Flash point of JBL showed great improvement over the CJO and thus justified the chemical modification of the oil.

The ISO viscosity classification is recommended for industrial applications. The reference temperature of 40 °C represents the operating temperature in machinery. Each subsequent Viscosity grade (VG) within the classification has approximately a 50% higher viscosity, whereas the minimum and maximum values of each grade ranges ±10% from the mid-point. Lubricants are usually identified by their grades. Table 7 presents specification of ISO viscosity grades and the properties of JBL. These specifications were earlier used by Mohammed et al. [39].

Table 7 ISO viscosity grade requirement and properties of JBL (at 140 °C, 4:1 JME–TMP mole ratio)

Property	ISO VG32 [39]	ISO VG46 [39]	ISO VG68 [39]	ISO VG100 [39]	JBL
Viscosity (Cst)					
40 °C	>28.8	>41.1	>61.4	>90	39.45
100 °C	>4.1	>4.1	>4.1	>4.1	8.51
Viscosity Index (VI)	>90	>90	>198	>216	204
Flash Point (°C)					178
Pour point (°C)	<−10	<−10	<−10	<−10	−12

Conclusion

Production of environmentally adapted lubricant basestock through transesterification of JME and TMP using calcium hydroxide catalyst had been achieved. The ester group was confirmed by FTIR. The effects of process parameters such as time, temperature and mole ratio on the synthesis of JBL indicated that temperature and mole ratio were the main factors that affected the transesterification process. After about 3 h of reaction, there was no remarkable increase in yield. It can be concluded that the optimal condition for the esterification of TMP ester was found at 3 h, 140 °C and JME:TMP of 4:1 at 1% wt/wt catalyst loading. Gibbs free energy indicated that the reaction was spontaneous with a second order rate constant of $1.00\text{E}-01$ $(\%\text{wt/wt min °C})^{-1}$ and kinetic energy of 13.57 kJ/mol. The pour point for JBL was −12 °C, viscosity of 39.45 and 8.51 cSt at 40 and 100 °C, respectively, with the Viscosity Index of 204. JBL properties complied with ISO VG 32 standard. The resulting properties indicated at the conditions of the experiment, that JBL has a high potential for production of lubricants with slight modifications.

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