Synthesis of Ethylene Glycol Diesters as Bio-Lubricant from *Jatropha* Methyl Esters

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ABSTRACT

The synthesis of ethylene glycol diesters as bio-lubricant was achieved via Trans- esterification reaction of *Jatropha* Methyl Ester (JME).The experimental strategy consists from two Transesterification reaction steps.At first step,*Jatropha* oil was extracted and characterized and then converted into JME. Then JME was converted to biolubricant at 120^{o}C, molar ratio of ethylene glycol to JME was 1:3.5 through 2.5 hr. and sodium meth-oxide was used as a catalyst was 0.8% w/w of total reactants. The physicochemical properties of the bio-lubricant were investigated. Kinematic viscosity at 40 ^{o}C was 16 cSt, kinematic viscosity at 100 ^{o}C was 4.54 cSt, viscosity index was 195.83 and the pour point was 18^{o}C.FTIR spectrum for JME to confirm the ester group was 1741cm^{-1}while for bio-lubricant was 1743cm^{-1}.It was found that the synthesis bio-lubricant data agree with petroleum base lubricant that reported by previouswork investigation.

***Keywords*: JME; Transesterification; Ethylene Glycol; Bio- lubricant**

اصطناع استرات الايثلين جلايكول الثنائية كزيت تشحيم حيوي من استرات ميثيل الجاتروفا

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ملخص الدراسة

تم اصطناع استرات الايثلين جلايكول الثنائية كزيت تزييت حيوي عن طريق تفاعل الاسترة التحويلية لاسترات ميثيل الجاتروفا. استراتيجية التجربة اشتملت على خطوتين من تفاعل الاسترة التحويلية. الخطوة الاولي تم استخلاص زيت الجاتروفا حيث تم دراسة خصائصه ثم حول الى استرات ميثيل الجاتروفا. حولتاسترات ميثيل الجاتروفا الى الزيت الحيوي عند درجة حرارة 120م° وذلك بنسبة مولية للايثلينجلايكول الى استرات ميثيل الجاتروفا (3.5:1)وكان زمن التفاعل 2.5 ساعة باستخدام ميثو اكسيد الصوديوم كعامل حفاز بنسبة 0.8% من الوزن الكلي للمتفاعلات. درست الخصائص الفيزيوكيميائية للزيت الحيوي مثل اللزوجة الكاينماتيكية عند 40 م° هي 16 سنتي ستوك ، واللزوجة الكينماتيكية عند100 م° هي 4.54 سنتي ستوك ، ومعامل اللزوجة هو 195.83 ، ونقطة الانسكاب هي 18 م°. وايضا تم إجراء التحليل الطيفي بواسطة الاشعة تحت الحمراء لاستراتجاتروفا الميثيل للتأكد من مجموعة الاستر كان عند طول موجي 1741 سم$^{-1}$ بينما الطول الموجي للزيت الحيوي 1743 سم$^{-1}$. وجد ان نتائج الزيت الحيوي الذي تم اصطناعه تتفق مع نتائج زيت الاساس البترولي في الدراسات السابقة.

الكلمات المفتاحية:استرات جاتروفا الميثيل ، الاسترة التحولية ، الايثلين جلايكول ، الزيت الحيوي

INTRODUCTION

The depletion of the fossil fuel as a source of lubricants followed by increasing the price of mineral and synthesis lubricants due to theirhigh consumption by consumers. In addition to their non-biodegradability and toxicity nature which can be lead to environmental pollution oriented the researchers to find alternative, renewable and friendly substitutes such as vegetable oils.

Lubricants are complex formulated products consistingof 70 to 90% base stocks with the right physical characteristics, mixed with functional additives to optimize the physical properties in order to meet a series of performance specifications. The base stocks can be mineral, synthetic or re-refined apart from vegetable oils (Srivastavaand Sahai, 2013).

The term bio-lubricants apply to all lubricants that are both rapidly biodegradable and non-toxic to humans and aquatic environments (Salimon*et al.*, 2010).Bio-lubricants formulated from plant oils should have some advantages derived from the chemistry of the base stocksuch ashigher lubricity leading to lower friction losses, yielding more power, better fuel economy,Lower volatility resulting in decreased exhaust emissions,Higher viscosity indices,Higher shear stability,Higher detergency eliminating the need for detergent additives,Higher dispersancy and Rapid bio-degradation and hence decreased environmental/Toxicological hazards(Salimon*et al.*, 2010).

Vegetable oils are viable and good substitute's resources due to their environmentalfriendly, non-toxic and readily biodegradable nature (Hsien, 2015).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 (Menkiti*et al.*, 2017).

MATERIALS AND METHODS

Materials and Reagents

The materials and reagents used in carrying out the study are as follows:*J.curcas*seeds, Anhydrous Methanol, Sodium hydroxide pellets, Potassium hydroxide, Phenolphthalein, Ethylene glycol, Sodium metal, Ethanol, Oxalic acid, Glacial acetic acid, starch, chloroform, sodium thiosulphate, potassium iodide, Hydrochloric acid. *J.curcas* seeds were obtained from National Oil Production Research Institute (NOPRI) where it was collected from western part of Sudan (Abu Karshola).Also all chemicals and reagents were taken from department of Chemical Engineering and NOPRI, University of Gazira. Whilethe instruments and equipment's used aremechanical press machine, FTIR apparatus, pour point apparatus, heating mantle, viscometers, oil Bath at 40^{o}C and at 100^{o}C,water bath, analytical balance,conical flasks, graduated cylinders, 25 and 50 ml. beakers, three necksround bottom flasks, magnetic stirrer, retort stand and clamps, condensers with ground glass joints, thermometer capable of measuring both negative andpositive temperatures, pipettes and burette, mechanical stirrer and test tubes.

Oil Extraction

Dried *J. Curcas* seeds were cracked to reduce their sizes by cracker machine. Then they were pressed using laboratory oil expeller (OEKO TEK, IBG MONFORTS, Type CA 59 G, 2006, Machine No.20201550.Germany. Then extracted oil was filtered to remove suspendedmaterials. And its physicochemical properties such as FFA%, acidity, saponification value, peroxide value

and refractive index were determined according to AOCS Ca 5a-40, AOCS 5a-40(1989), BS68426,AOCS Cd8-53(1989) and AOCS Cc7-25 respectively.

Synthesis of JME

The experiments were carried out in 1000 ml three-neck round bottom flask, equipped with reflux condenser;the flask was placed on a hot plate equipped with magnetic stirrer and temperature controller. Drying of JCO was carried out by heating the oil to 110°C, then cooling to 65°C. After drying, the JCO was subjected to JME production using one step base catalyzed Transesterification reaction (AbdElrahman, 2017). The reaction was carried out for 60minute. The reaction mixture was cooled down to ambient temperature and the resulting two layers were separated. The upper layer contained a solution of methyl esters. The experiment was repeated three times and actual yield was calculated in each time as shown in Table(2).And then it was subjected for further purification.The prepared JME was subjected to Fourier transform infrared spectroscopy analysis to confirm the ester group.

Synthesis of Bio-lubricant

It was achieved by Tran's esterification of the methyl ester with ethylene glycolin 250 ml three neck round bottom flask.The reaction was carried out at 120°C and the molar ratio of JME to ethylene glycol was1:3.5 for 2.5 hours (Bilal*et al*, 2013). Then sodium meth oxide as catalyst was0.8% from all reactants weight was added to the reaction mixture. The catalyst was prepared simply by dissolving 2.5 g of fresh clean sodium in 25 ml of methanol. Crude bio-lubricant was subjected to FTIR analysis in order to compare its spectrum with JME spectrum to confirm the occurrence of the reaction.

RESULT AND DISCUSSION

Characterization of *J. curcas*Crude Oil

The free fatty acids valueswere 2.05% and 2.53 %, the peroxide value was 2.64 meq/kg, refractive index was 1.4710, saponification value was 199.13 mg KOH/g oil and the average molecular weight was 863.08 g/mole as shown in Table (1).

Table 1. Characteristics of JatrophaCrude Oil

Property	Values
FFA%	2.05 – 2.53
Peroxide Value (meq/Kg)	2.64
Saponification Value (mg KOH/g oil)	199.13
Average Molecular Weight (g/mole)	863.08
Acid Value	4.09
Refractive Index	1.4710

The actual yields were found to be 88.84%, 86.47%and 85.89% respectively as shown in Table (2). And that may be refer to the FFA % which was greater than 2% and this lead to soap formation and to decrease biodiesel yield.

Table 2. Actual Yield of Prepared JME

Sample No.	*J.Curcas* oil weight, g	JME weight, g	Actual yield, %
1.	430.39	380.80	88.480
2.	139.00	117.60	86.470
3.	487.37	414.60	85.890

The prepared biodiesel was subjected to FTIR analysis.As shown in Figure(1),the JME indicates a peak at3344.57 cm^{-1} conforming the stretching and bending vibration of O-Hbonds due to the presence of water molecules.The anti-symmetricand symmetric stretching vibrations of C-H in - CH_2 and - CH_3 groupscan be confirmed by the presence of peaks at 2924.09 cm^{-1} and2856.58 cm^{-1} respectively.

The strong peak present at 1741 cm^{-1} isattributed to the presence of C=O stretching vibration of carbonylgroups that is present in the JME.Thisobservation is in consistent agree with FTIR analysis that reportedby(Sharma*et al.*, 2016), which also supportsthat synthesized product is biodiesel.

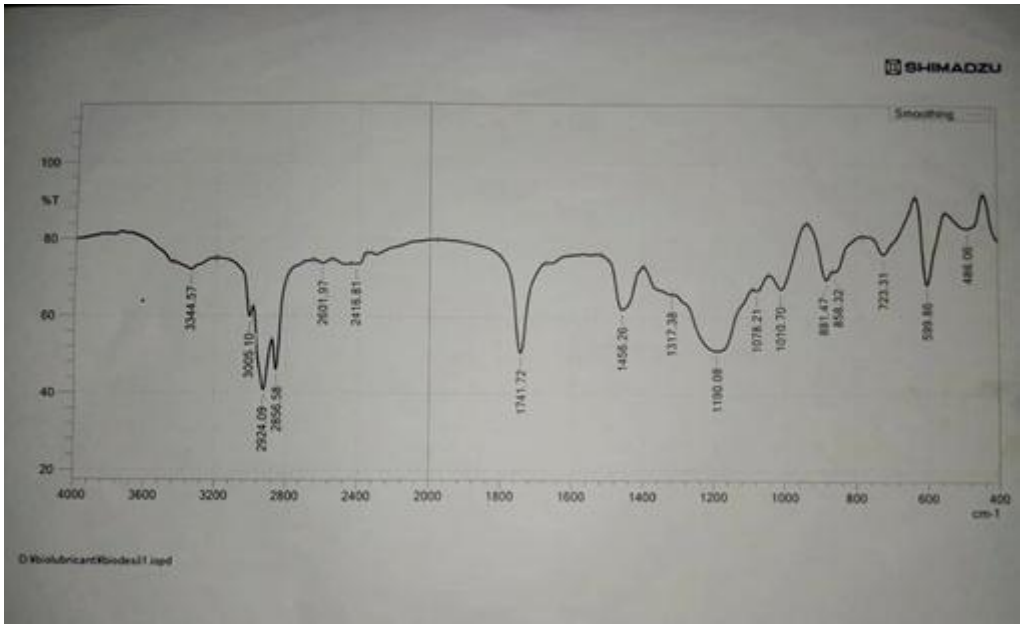

Figure 1. FTIR Spectrum for JME

The physiochemical properties of synthesis bio-lubricant such as kinematic viscosity at 40°C, kinematic viscosity at 100°C, viscosity index and pour point were investigated and they were found to be 16 cSt, 4.54 cSt, 195.83 and 18°C respectively as shown in Table (3). The kinematic viscosity at 100°C and the viscosity index agree with ISO VG-46 standard.while the Kinematic viscosity at 40°C, kinematic viscosity at 100°C, viscosity index and pour point were 55.17 cSt, 10.96 cSt,195.22 and -7 °C respectively for synthesis bio-lubricant according toBilal*et al.*, 2013, only the value of viscosity index agree with this work. Thus the different between the synthesis lubricants according to Bilal et al., 2013and this work perhaps refer to the different in the extraction methods and thepreparation of JME in both studies.Also the value of pour point was very high and that may be referred to the fact that the synthesis mixture was crude and it has not be refined yet.

Table 3.Characterization of Bio-lubricant

Property	*J.Curcas* oil weight		Hydraulic ISO-46	Petroleum based Petroleum based lubricant
	Current study	Bilal, S *et al*, 2013		
Viscosity@40°C, cSt	16	55.17	>41.4	10.801

Viscosity@100^{o}C, cSt	4.54	10.96	>4.0	3.136
Viscosity index	195	105.22	> 90.0	165.4
Pour point	18	-7	-10	-9

Fourier transforms infrared (FTIR) spectroscopy of JME and *J.Curcas*biolubricant has also been conducted which is shown in Figure (1) and Figure (2). The FTIR spectrum of the carbonyl group of JME is shifted from 1741cm^{-1} to 1743 cm^{-1}, which indicates that the number of carbonyl group is increased and it clearly shows that JME containing only one carbonyl group compared to baseline *J.Curcas*biolubricant, which originally contains two carbonyl groups which support that synthesized product is the biolubricant (ethylene glycol diesters).

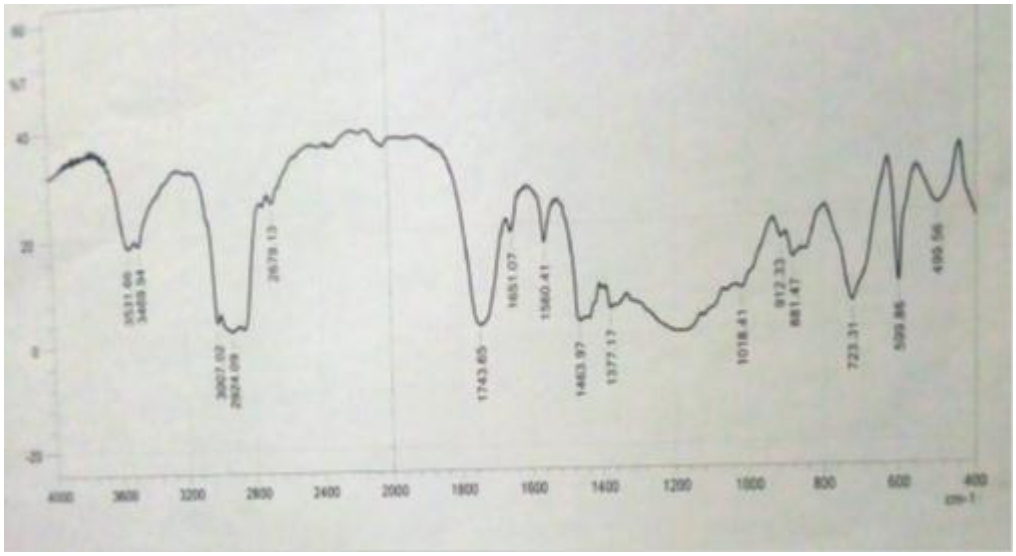

Figure 2. FTIR Spectrum for Biolubricant

CONCLUSION

The present study was succeeded in extracting oil from *J.Curcas*seeds and converting *J.Curcas* oil to JME, then converting JME into bio-lubricant. The synthesis bio-lubricant was subjected to FTIR analysis and the physicochemical properties such as kinematic viscosity at 100^{o}C, kinematic viscosity at 40^{o}C, viscosity index and pour point were investigated. The FTIR analysis in figures 1 and 2 shownthe carbonyl group was shifted from 1741 cm^{-1} inJME to 1743 cm^{-1} in synthesis biolubricant due to increase the number of carbonyl groups in the latter in which will be confirmed the formation of the synthesis lubricant.

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