

PAPER • OPEN ACCESS

## Intensification of biolubricant synthesis from waste cooking oil using tetrahydrofuran as co-solvent

To cite this article: T W Putra *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **845** 012009

View the [article online](#) for updates and enhancements.

### You may also like

- [Electrostatic atomization minimum quantity lubrication machining: from mechanism to application](#)  
Wenhao Xu, Changhe Li, Yanbin Zhang et al.
- [Synthesis Biolubricant By Esterification Of Castor Oil \(\*Jatropha Curcas L\*-Oil\) With Chlorate Acid Catalyst](#)  
Agus Rochmat, Aslan Dudayev Alfaruqi, Saefuri et al.
- [Effect of Nano Particles on Tribological Behavior of Reciprocating Air Compressor Oil Using Fourball Tribometer: An Experimental Investigation](#)  
P. Chenga Reddy and S. Arumugam



**ECS**  
The  
Electrochemical  
Society  
Advancing solid state &  
electrochemical science & technology

**DISCOVER**  
how sustainability  
intersects with  
electrochemistry & solid  
state science research

## Intensification of biolubricant synthesis from waste cooking oil using tetrahydrofuran as co-solvent

T W Putra<sup>1</sup>, R Hardiansyah<sup>1</sup>, M R Lubis<sup>1</sup>, and M D Supardan<sup>1\*</sup>

<sup>1</sup>Departement of Chemical Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh-23111, Indonesia

E-mail: m.dani.supardan@unsyiah.ac.id

**Abstract.** In this study, biolubricant was synthesized through two stages of transesterification. The first transesterification was the reaction between waste cooking oil and ethanol using sodium hydroxide as catalyst to produce fatty acid ethyl esters (FAEE). The second transesterification was the reaction between FAEE and 1-octanol using potassium hydroxide as catalyst with tetrahydrofuran as co-solvent to produce fatty acid octyl esters (biolubricant). This study was focused on the effect of tetrahydrofuran as co-solvent in the second transesterification. Biolubricant yield of 94.42% was obtained at reaction conditions (temperature of 125°C, time of 180 min, reactant molar ratio of 1:4, catalyst amount of 1%-w/w, vacuum pressure of 100 mmHg and co-solvent amount of 25%-w/w). The physico-chemical properties of biolubricant were kinematic viscosities of 10.47 mm<sup>2</sup>/s and 2.75 mm<sup>2</sup>/s at 40°C and 100°C, viscosity index of 103 and acid number of 0.62 mg KOH/g.

### 1. Introduction

The world demand for lubricating oil as protectors of engines caused by friction, heat corrosion has increased in this era [1]. The needs of this lubricating oil are almost entirely fulfilled by petroleum-based lubricating oil (Lubricant). Demand for lubricants continuously increasing furthermore cause problems on petroleum-based energy and environmental pollution. Every year about 55% of residual lubricants have polluted the environment which included soil, water and air [2]. Therefore, renewable and environmentally friendly lubricants are needed to solve these problems.

The development of the synthesis of environmental friendly-based lubricating oil or biolubricant as a substitute for petroleum-based lubricant is still being carried out. Biolubricant is an environmental friendly lubricating oil because it can decompose naturally by microorganisms (biodegradable) and low toxicity [3]. Biolubricant is also renewable because it can be made from vegetable oils such as palm oil, coconut oil, soybean oil, castor oil and sunflower oil [4].

The biolubricant can be synthesized by several methods such as transesterification, selective hydrogenation and epoxidation [5]. Transesterification is the most widely used method and recommended because it can produce yield higher than 90% [4]. Furthermore, the advantage of transesterification is increased oxidative stability so that the biolubricant is not easily damaged by oxidation. However, transesterification requires a high reaction temperature which causes increase energy consumption and production cost [5]. Therefore, the transesterification method still needs to be developed more.

---

\* To whom any correspondence should be addressed.



At this time, the production and application of biolubricant are still limited. In fact, The energy shortage, environmental pollution and technological advances in the automotive and manufacturing in industries are increasingly demanding the use of biolubricant [6]. This problem is caused by the production of biolubricant requires high production cost. This affects biolubricant price which can be more expensive than lubricant. Furthermore, it will be an obstacle in order to produce biolubricant which can be competing for the economic value of commercial lubricant's [7].

The efforts to produce biolubricants with simpler and cheaper processes continue to be developed at this time. The use of cooking oil waste (WCO) as raw material for biolubricants has very important and interesting effects such as to reduce the cost of biolubricant production because its' price is cheaper than other vegetable oils; and to reduce environmental pollution because WCO is waste [8]. Raw material cost takes around 70-80% of total production costs and WCO prices are 30-60% cheaper than other vegetable oils [9]. The study of biolubricant production from WCO using transesterification was carried out by Wang et al. produce biolubricant yields of 85.7%. Studies on biolubricant production from WCO still need to be developed in order to obtain higher yields [9].

The application of co-solvent in the synthesis of biolubricant is still very rare. At this time, the application of co-solvent especially tetrahydrofuran (THF) is still focused on biodiesel synthesis [10]. Co-solvent can accelerate the reaction by increasing the solubility of oil and alcohol so that oil and alcohol can be completed reaction and increase yield [11]. Fransiska et al. have recommended the application of THF as co-solvent in the transesterification. THF has a good ability to dissolve fatty acids (triglycerides) and alcohol. In addition, THF has a low toxicity, boiling point of 67°C which can be separated easily and the price is relatively cheaper than other co-solvents [12].

This study purposes to obtained the intensification of biolubricant synthesis from WCO using THF as co-solvent. This study is expected to help develop the production of biolubricant to be better. Thus, the prospect of biolubricant to substitute lubricant is getting bigger.

## 2. Methodology

### 2.1. Equipments and Chemicals

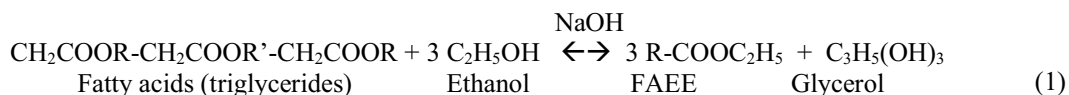
The raw material was the WCO from five times frying. The WCO was obtained from palm oil based cooking oil. Cooking oil was used to fry fish, tofu and tempeh for five times. The chemical compounds used were ethanol 96%, sodium hydroxide (NaOH), Potassium hydroxide (KOH), THF ACS reagent 99% (Merck Indonesia), 1-Octanol 99% (Merck Indonesia). Meanwhile, the equipments used were hot plate (Yamato MH-800), vacuum pump (Rocker 3000), Three neck flask 1000 mL (Duran), reflux condenser glassed, magnetic stirrer, rubber tube, thermometer 150°C, beaker glass 500 mL (pyrex), erlenmeyer 250 mL (pyrex).

### 2.2. Biolubricant synthesis

Two stages of transesterification were carried out for fatty acid octyl esters (biolubricant) synthesis. The first transesterification was the synthesis of fatty acid ethyl esters (FAEE). The second transesterification was the synthesis of biolubricant.

#### 2.2.1. The first transesterification (synthesis of FAEE).

The first transesterification was the reaction between WCO and ethanol to produce FAEE as below:

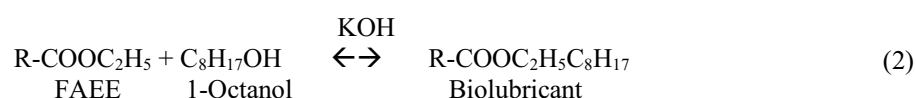


The free fatty acid (FFA) of WCO was 1.06% so that could be directly transesterification but if FFA of WCO was 2%, it should be esterification before transesterification [13]. The synthesis of FAEE was done in a three neck flask 1000 mL with reflux condenser. WCO was added ethanol with

molar ratio (1:6) and NaOH catalyst amount of 0.5%-w/w. The mixture was reacted at temperature of 65°C for 90 min with stirring. The result of reaction was moved into separating funnel and set aside within 18 h so that formed two layers. The upper layer was FAEE and bottom layer was glycerol. The FAEE and glycerol were separated. The FAEE was washed with hot water (50°C) to remove residual ethanol, catalyst and soap. The FAEE was purified at temperature of 110°C to remove residual water and ethanol. Finally, the purified FAEE was obtained to be raw material for the second transesterification.

### 2.2.2. The second transesterification (synthesis of biolubricant).

The second transesterification was the reaction between FAEE and 1-octanol to produce biolubricant as below:



The synthesis of biolubricant was done in three neck flask 1000 mL with the reflux condenser which was connected with a vacuum pump. The FAEE was added 1-octanol with molar ratio (1:4) and KOH catalyst amount of 1%-w/w. The mixture was reacted at conditions (temperature = 65, 85, 105, 125 and 135°C, time = 60, 120, 180, 240 and 300 min, THF = 0, 25, and 50%-w/w). The mixture was stirred with 300 rpm at vacuum pressure of 100 mmHg. The result of reaction was moved into separating funnel. The biolubricant was washed with hot water (80°C) to remove residual 1-octanol, catalyst and soap. The biolubricant was then purified at temperature of 200°C to remove residual water and 1-octanol. Finally, the purified biolubricant was collected for analysis.

### 2.3. Analysis of biolubricant

Biolubricant were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) Shimadzu Prestige 6400. This analysis was carried out to determine the functional groups of fatty acid octyl ester based on the wavelength. So the compounds formed in product could be known by comparing them with functional groups in the related references. Basically, the FTIR analysis is carried out to prove that the reaction has been completed to produce the biolubricant.

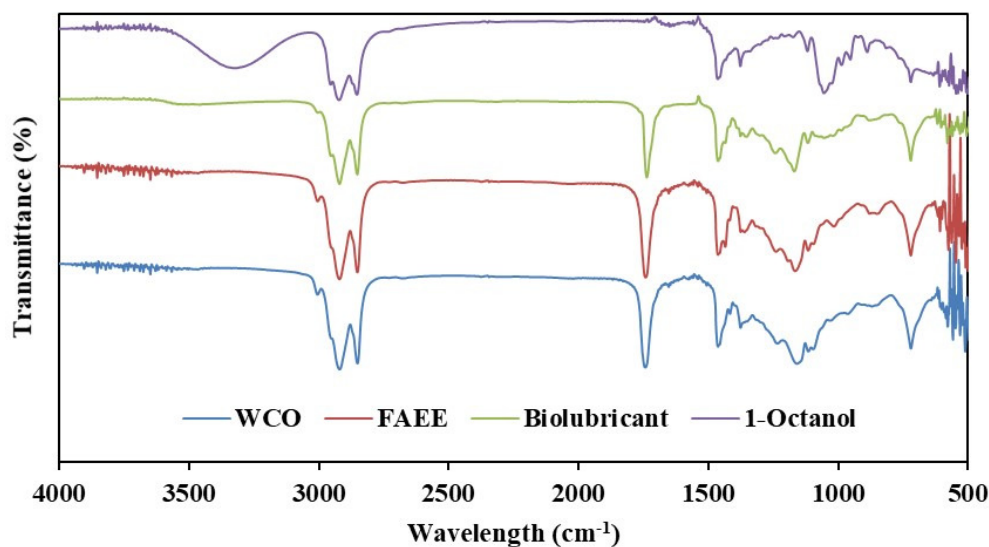
### 2.4. Determination of the physico-chemical properties of biolubricant

The physico-chemical properties of biolubricant analyzed in this study were density, kinematic viscosity at 40°C and 100°C, viscosity index and acid number. Density was determined by pycnometer 5 mL (IWAKI) according to the ASTM D1217. Kinematic viscosity at 40°C and 100°C was determined by ostwald viscometer according to the ASTM D445 standard method. Viscosity index was calculated according to the ASTM D2270 standard method. Acid number was determined by titration method according to the D974 standard method.

## 3. Results and discussion

### 3.1. Functional groups of biolubricant

The FTIR analysis results obtained spectrum is given in Figure 1. FTIR spectrum compares functional groups of 1-octanol, WCO, FAEE and biolubricant as shown in Table 1. Figure 1 and Table 1 show the difference of functional groups between 1-octanol, WCO, FAEE and biolubricant. The hydroxide group (-OH) as alcohol group appears at 3323.35 cm<sup>-1</sup> found in 1-octanol. It is not found in WCO, FAEE and biolubricant. The absence of the -OH in biolubricant indicates that the reaction has converted 1-octanol to biolubricant successfully. It also indicates that biolubricant does not contain the residual 1-octanol KOH catalyst and water. The purification has been successful. The presence of the -OH is not expected in biolubricant. The smaller the -OH in biolubricant indicates that reaction process was close to completion [3].



**Figure 1.** FTIR spectrum of waste cooking oil (WCO), fatty acid ethyl esters (FAEE), fatty acid octyl esters (biolubricant) and 1-octanol.

**Table 1.** Function group of waste cooking oil (WCO), fatty acid ethyl esters (FAEE), fatty acid octyl esters (biolubricant) and 1-octanol.

Function group	Reference	Wavelength (cm <sup>-1</sup> )			
		WCO	FAEE	Biolubricant	1-Octanol
-OH (alcohol)	3326 <sup>a</sup>	-	-	-	3323.35
C=O (ester)	1744 <sup>a</sup>	1743.65	-	-	-
	1741 <sup>b</sup>	-	1741.72	-	-
	1738 <sup>c</sup>	-	-	1737.86	-
C-O (ester)	1168 <sup>b</sup>	1159.22	1166.93	1170.79	-
	1056 <sup>c</sup>	-	-	1056.99	-
C-O-H (Alcohol)	1050 <sup>d</sup>	-	-	-	1053.13

<sup>a</sup>)Heikal et al. [3]

<sup>b</sup>)Ivan-Tan et al. [15]

<sup>c</sup>)Chowdhury et al. [8]

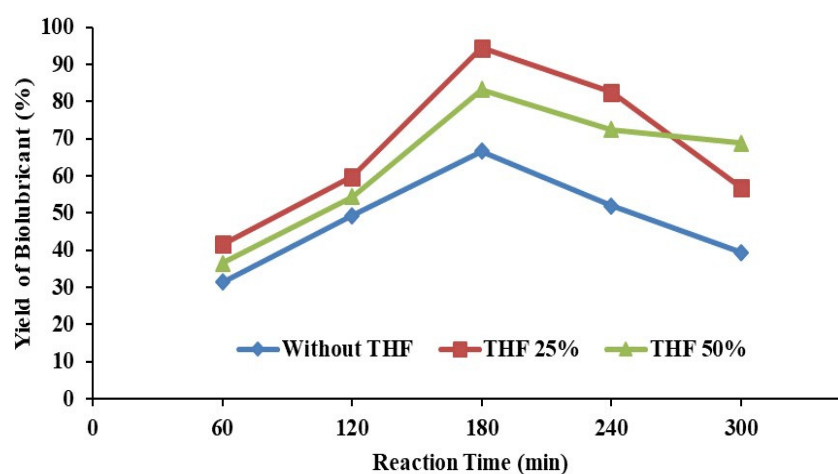
<sup>d</sup>)Tahari et al. [16]

The ester group (C=O) appears in WCO at 1743.65 cm<sup>-1</sup>, FAEE at 1741.72 cm<sup>-1</sup> and biolubricant at 1737.86 cm<sup>-1</sup>. The change at 1743.65 cm<sup>-1</sup> to 1741.72 cm<sup>-1</sup> indicates that the FAEE is obtained from the first transesterification. There is a significant change from 1741.72 cm<sup>-1</sup> to 1737.86 cm<sup>-1</sup> indicates that the fatty acid octyl esters (biolubricant) is obtained from the second transesterification. The wavelength of 1737.86 cm<sup>-1</sup> is the specific wavelength of C=O (ester) group for fatty acid octyl esters because it only appears in 1-octanol based biolubricants [8,14].

The function group of C-O (ester) also appears in WCO at 1159.22 cm<sup>-1</sup>, the FAEE at 1166.93 cm<sup>-1</sup> and biolubricant at 1170.79 cm<sup>-1</sup>. But, the C-O (ester) at 1056.99 cm<sup>-1</sup> only appears in biolubricant. The wavelength of 1056.99 cm<sup>-1</sup> is the specific wavelength of C-O (ester) group for 1-octanol based biolubricants [8,14].

### 3.2. Effect of THF and reaction time on yield of biolubricant

The effect of THF and reaction time on yield of biolubricant at the temperature reaction of 125°C is shown in Figure 2. The result shows that reaction time can increase and decrease yield of biolubricant as well as shown in Figure 2. The reaction time of 60 to 180 min can increase yield of biolubricant because the FAEE and 1-octanol have time to react completely. While at the reaction time of 240 and 300 min, the yield of biolubricant obtained tends to decrease. This decrease is because the reaction has reached the equilibrium, at reaction time of 180 min. Furthermore, this decrease is also caused by the formation of a few soaps at high reaction temperature during the longer of reaction time [15]. In this study, the optimum reaction time obtained is 180 min which the yields of biolubricant obtained are 66.57% (without THF), 94.42% (THF 25%) and 83.25% (THF 50%).

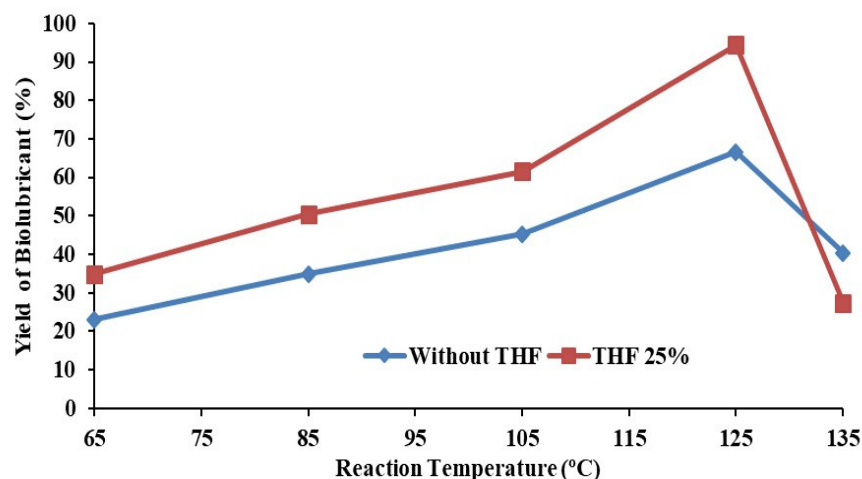


**Figure 2.** Effect of THF and reaction time on yield of biolubricant (molar ratio of FAEE:1-Octanol = 1:4, temperature = 125°C, catalyst 1%-w/w, vacuum pressure 100 mmHg).

The presence of THF can increase yield of biolubricant from 66.57% (without THF) to 94.42% (THF 25%). THF can increase yield of biolubricant by increase the solubility of FAEE and 1-octanol so that the reaction becomes more effective. But, the addition of THF excessively can also decrease yield of biolubricant from 94.42% (THF 25%) to 83.25% (THF 50%). The presence of THF excessively can disturb particle reaction collision between FAEE and 1-octanol. This is due to the effect of excessive dilution of THF [12]. A similar trend was reported by Satriana et al. [17] for glycerolysis reaction. In this study, the optimum addition of THF obtained is 25%-w/w of FAEE.

### 3.3. Effect of THF and reaction temperature on yield biolubricant

The result is obtained that reaction temperature can increase yield of biolubricant at time reaction 180 min as shown Figure 3. The reaction temperature of 65 to 125°C can increase yield of biolubricant from 23.06 to 66.57% (without THF) and 34.94 to 94.42% (THF 25%). This increase is due to the increasing reaction temperature which can increase reaction rate and accelerate reactant particle collisions. At the temperature of 135°C, yield of biolubricant has decreased from 66.57 to 40.36% (without THF) and 94.42 to 27.42% (THF 25%). This is due to 1-octanol has reached the boiling point at temperature of 135°C and vacuum pressure of 100 mmHg [18]. The evaporation of 1-octanol and THF can decrease driving force of reaction so that resulted yield of biolubricant is decreased [15]. In this study, the highest yield of biolubricant is obtained at reaction temperature of 125°C.



**Figure 3.** Effect of THF and reaction temperature to yield of biolubricant (molar ratio of FAEE:1-Octanol = 1:4, time = 180 min, catalyst 1%-w/w, vacuum pressure 100 mmHg).

#### 3.4. Physico-chemical properties of biolubricant

The physico-chemical properties of biolubricant include density (40°C), kinematic viscosity (40°C), kinematic viscosity (100°C), viscosity index and acid number as shown in Table 2. Table 2 shows the comparison of biolubricant and lubricant (ISO VG 10). Kinematic viscosity of biolubricant is higher than lubricant. Viscosity index of biolubricant is also higher than lubricant. These results indicate that lubricating biolubricant is better than lubricant. But acid number of biolubricant is higher than lubricant. This is affected by vegetable-based oil sources that contain the high FFA. Another reason is there is no additive added in biolubricant which makes it easily oxidized.

**Table 2.** Physico-chemical properties of biolubricant.

Physico-chemical properties	Biolubricant	Lubricant (ISO VG 10)
Density at 40°C (g/mL)	0.874	0.888
Kinematic viscosity at 40°C (mm <sup>2</sup> /s)	10.47	10
Kinematic viscosity at 100°C (mm <sup>2</sup> /s)	2.75	2.60
Viscosity index	103	90
Acid number (mg KOH/g)	0.62	0.30

#### 4. Conclusion

The intensification of biolubricant synthesis from WCO using THF as co-solvent was successfully obtained. The specific function group of C=O (ester) and C-O (ester) from fatty acid octyl esters (biolubricant) was obtained at 1737.86 cm<sup>-1</sup> and 1056.99 cm<sup>-1</sup> respectively. The highest yield of biolubricant in this study was 94.42% in reaction conditions (THF 25%, 125°C, 180 min and 100 mmHg). The optimal presence of THF as co-solvent had a significant effect on the quality and quantity of biolubricant. The physico-chemical properties of biolubricant were better than lubricant (ISO VG 10).

## References

- [1] Widyawati Y, Suryani A and Romli M 2014 *Int. J. Renew. Energy Dev.* **3** 188-
- [2] Madankar C S, Dalai A K and Naik S N 2013 *Ind. Crops Prod.* **44** 139
- [3] Heikal E K, Elmelawy M S, Khalil S A and Elbasuny N M 2017 *Egypt J. Pet.* **26** 53
- [4] Panchal T M, Patel A, Chauhan D D, Thomas M and Patel J V 2017 *Renew. Sustain. Energy Rev.* **70** 65
- [5] Syahir A Z, Zulkifli N W M, Masjuki H H, Kalam M A, Alabdulkarem A, Gulzar M, Khuong L S and Harith M H 2017 *J. Clean. Prod.* **168** 997
- [6] Panchal T, Chauhan D, Thomas M and Patel J 2015 *Ind. Crops Prod.* **63** 48
- [7] Gryglewicz S, Stankiewicz M, Oko F A and Surawska I 2006 *Tribol. Int.* **39** 560
- [8] Chowdhury A, Mitra D and Biswas D 2013 *J. Chem. Technol. Biotechnol.* **88** 139
- [9] Wang E, Ma X, Tang S, Yan R, Wang Y, Riley W W and Reaney M J T 2014 *Biomass and Bioenergy* **66** 371
- [10] Guan G, Sakurai N and Kusakabe K 2009 *Chem. Eng. J.* **146** 302
- [11] Supardan M D, Adisalamun, Lubis Y M, Annisa Y, Satriana and Mustapha W A W 2017 *Pertanika J. Sci. & Technol.* **25**, 1203
- [12] Fransiska F, Felicia and Taslim 2014 *Proc. of The 5<sup>th</sup> Sriwijaya Int. Seminar on Energy and Environmental Science and Technology (Palembang, Indonesia, 10-11 Semptember 2014)* Vol 1 27
- [13] Abdullah N H, Hasan S H and Yusoff N R M 2013 *Int. J. Mater. Sci. Eng.* **1** 94
- [14] Chowdhury A, Chakraborty R, Mitra D and Biswas D 2014 *Ind. Crops Prod.* **52** 783
- [15] Ivan-Tan C T, Islam A, Yunus R and Taufiq-Yap Y H 2017 *J. Clean. Prod.* **148** 441
- [16] Tahari M N A, Samidin S, Yarmo M A, Salih N and Salimon J 2015 *Malaysian J. Anal. Sci.* **19** 118
- [17] Satriana, Arpi N, Supardan, M D, Gustina, R T and Mustapha W A W 2018 *AIP Conf. Proc.* **1940** 020100
- [18] Liley P E, Thomson G H, Daubert T H and Buck E 1997 *Perry's Chemical Engineers' Handbook 7<sup>th</sup> Edition* ed R H Perry et al. (United States of America: McGraw-Hill) section 2 27