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BLENDING OF VEGETABLE OILS AND CHEMICAL MODIFICATION BY EPOXIDATION FOLLOWED BY OXIRANE RING-OPENING REACTION

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ABSTRACT

In this paper, vegetable oils as refined soybean oil, refined sunflower oil and their blends of different proportions were investigated for blending and epoxidation followed by oxirane ring-opening reaction. The physicochemical properties such as viscosity, acidity value, iodine value and saponification value were reported. From the results, the blend of vegetable oils with mass ratio of 80:20 (sunflower oil: soybean oil) had higher viscosity index than individual vegetable oil, as well as suitable acidity and saponification value. However, the relatively high iodification of this blend indicated that this blend had a low oxidation stability. Hence, this mixture has been continually exposed to epoxidation reaction with the purpose of removing the presence of double bond C=C followed by oxirane ring-opening reaction. The results indicated that temperature, time of reaction, molar ratio H_2O_2/C=C influenced significantly on iodine value of obtained blend. The following conditions in epoxidation step: CH_3COOH/C=C 1:1; time of reaction 7h, temperature of reaction 60^{o}C, stirring speed 500 rpm and H_2O_2/C=C 3:1 could reduce effectively iodine value, from 129.6 to 6.9. In the oxiranering-opening reaction, n-butanol was used as reagent, and the final product had higher viscosity compared to epoxidized blend.

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1 INTRODUCTION

Lubricants consist of about 70-99% of base oil and 1-30% additives. Over 95% of base oil has origin from mineral oil (Salimon *et al.,* 2012). Depletion of crude oil and environmental concerns leads to increasing interest in renewable and biodegradable lubricants. In this term, vegetable oil is an alternative to mineral base oil of lubricant. Most of vegetable oils are made up of triglycerides with similar length of fatty acids, between 14 and 22 carbon atoms, having different degree of unsaturation (Fox *et al.,* 2007). In comparison with mineral base oil, vegetable oils have higher flash point, higher viscosity index, higher lubricity and lower evaporation loss. However, vegetable oil also has certain drawbacks that need to be improved, for example, limited thermo-oxidative and hydrolytic stabilities (Campanella *et al.,* 2010). Efforts have been made to improve their oxidative stability such as selective hydrogenation of unsaturated oil (Lathi *et al.,* 2007), epoxidation to convert double bond C=C into oxirane ring.

Blending of vegetable oils can bring about the advantage of improving viscosity index, acid value, saponification and iodine value (Marotrao *et al.,* 2012). However, the iodine value is notably high and need to be reduced. In the review of the authors, the epoxidation of a blend of vegetable oils was not investigated, although there were researches into this reaction of different pure vegetable oils.

In this study, physicochemical properties including viscosity, viscosity index, acid value, saponification and iodine value of different vegetable oils and their blends were analysed. After that, the epoxidation followed by oxirane ring opening of the suitable blended refined soybean and sunflower were carried out. Different composition of the blend as well as condition reaction such as chemical agents ratio, time and temperature of reaction were investigated.

2 METHODS

2.1 Determination of viscosity, viscosity index, acid value, iodine value and saponification value of pure oils and their blends with different ratios

Viscosity of pure refined soybean oil, sunflower oil at 40°C and 100°C were determined using Redwood viscometer. The blends were prepared in 10:90 to 90:10 of mass ratio, and their values of viscosity at 40°C and 100°C were measured again using the same viscometer. Viscosity index of the samples deduced from viscosity at 40°C and 100°C. The acid values, iodine values and saponification values of pure oils and the blends were measured by titrametric methods of Pearson.

2.2 Epoxidation of blend oil

Epoxidized oil of 100 g blend of soybean and sunflower oils with mass ratio at 20:80 was prepared by reacting the blend oil with mixture of CH_3COOH/H_2O_2. The product of the reaction was rinsed with water until complete removal of excess acid and then distilled to obtain epoxidized oil. The molar ratio of CH_3COOH/C=C in the reaction was 1:1 with 30 ml of CH_3COOH, stirring speed was 500 rpm.

The reation temperature varied between 40÷60°C, molar ratios H_2O_2/C=C were 1:1, 2:1, 3:1 alternately, time of reaction was investigated between 4 and 7h.

2.3 Oxirane ring-opening reaction of epoxidized blend oil

The reation was investigated on the obtained epoxidized oil in the conditions described in previous part using n-butanol reagents. The epoxidized oil was stirred with n-butanol at 90°C, then concentrated H_2SO_4 was dropped into the mixture gradually and temperature was raised to 100°C. The mixture was left for reaction in 3h, after that washed with distilled water and dried at 80°C under vacuum pressureto remove n-butanol and water. The product obtained was then compared to specified based oils in lubricating fabrication.

3 RESULTS AND DISCUSSION

3.1 Viscosity and Viscosity Index of pure oils and their blends in different ratios

Viscosity and Viscosity Index (VI) are ones of the most important properties of industrial lubricant. The VI range of mineral oil based lubricant is often 90-100. For very high viscosity index mineral oil based stocks, VI varies from 110 to 130. The appearance of Oxygen containing compounds in synthetic base oil increases VI to 120-160. As seen in Table 1, these two properties vary with respect to blended oil composition. The blend of refined sunflower oil and refined soybean oil with mass ratio of 80:20 had the highest VI of 235.71 among tested blends.The suitability of molecular structure in the two oils might be a reason of this phenomenon. Viscosity of the blend at 40°C and 100°C changed slightly with its composition and were near viscosity of pure oils. This might be because there is no significant difference in molecular structure of pure oils. The vegetable oils have mainly in their structure oleic and linoleic acid. Viscosity value of vegetable oils differs slightly because of their difference in saturated acid content (Talkit *et al.*, 2012).

Table 1: Viscosity and Viscosity Index of pure vegetable oils and their blends

Refined sunflower oil: Refined soybean oil (mass ratio)	υ at 40°C, cSt	υ at 100°C, cSt	VI
100:0	30.58	7.25	215.21
80:20	28.65	7.26	235.71
60:40	29.21	7.15	223.32
50:50	30.06	7.19	216.79
40:60	29.01	7.16	226.35
20:80	29.91	7.20	219.16
0:100	29.83	7.16	217.54

3.2 Acid value, iodine value and saponification value

The acid value of pure oils and blended oils are presented in Table 2. In lubricants, the presence of acidic compounds was not preferred because they are the source of gum and sludge besides causing corrosion. From the results, the mixture of refined sunflower oil and refined soybean oil at mass ratio of 80:20 had the smallest acidic value among the blended oils. The lower acidic value means that the mixture act as a better lubricating oil blend than others (Marotrao *et al.,* 2012).

Table 2: Acid value pure of vegetable oils and their blends

Refined sunflower oil: Refined soybean oil (mass ratio)	Acid value
100:0	0.048
80:20	0.062
40:60	0.094
0:100	0.126

Table 3: Saponification value of vegetable oils and their blends

Refined sunflower oil: Refined soybean oil (mass ratio)	Saponification value
100:0	196.49
80:20	194.95
40:60	191.19
0:100	191.92

Determination of saponification value is necessary to ascertain the fixed oil in lubricants. This saponification value is significant in animal oil or vegetable oil based lubricants because the mineral oil does not undergo saponification. Accordingly, saponification value of vegetable oil fits to be used as base oil in lubricants is 186-198 (Gawrilow, 2003). So, from Table 3, saponification value of all pure oils and blended oils was situated in this range.

Table 4: Iodine value of vegetable oils and their blends

Refined sunflower oil: Refined soybean oil (mass ratio)	Iodine value
100:0	129
80:20	129.6
40:60	130.8
0:100	132

Iodine value of vegetable oil fits to be used as base oil in lubricants is 94-126 (Gawrilow, 2003). As seen in Table 4, iodine value of sunflower oil is 129 and that of soybean oil is 132. The mixture of sunflower oil and soybean oil of 80: 20 (mass ratio) was 129.6. This value is higher than expected value applied in vegetable base oil lubricants. Hence, further studied related to the decrease of unsaturation degree of this oil mixture is needed.

3.3 Epoxidation reaction

3.3.1 Influene of reaction temperature on conversion of C=C bond

The reactions were carried out in the following conditions: reaction time of 4 h, molar ratio of H_2O_2/C=C of 1:1, molar ratio of CH_3COOH/C=Cof 1:1, stiring speed of 500 rpm. The reaction temperature was changed in the range 40÷60^{o}C and iodine value of obtained epoxidized product was determined. The results were displayed in Table 5.

Table 5: Iodine value of epoxidized produced at different reaction temperature

Temperature (^{o}C)	Iodine index (g I_2/100g)
40	89.8
50	84.1
60	52.6

Regarding Table 5, when the temperature rose from 40 to 60^{o}C, the iodine index decreased from 89.8 to 52.6. This indicated that unsaturation level of product dropped, and the conversion of C=C bond into oxirane ring increased. At 60^{o}C, the conversion of C=C bond was 59.41%.

Howerver, when the temperatureincreased continually to 70^{o}C, the catalyst (H_2SO_4) became a strong oxidant which boosted the polymer reaction. On the other hand, when the temperature exceeded over 80^{o}C, oxirane ring could be opened by the agent such as water or acid acetic in the reaction mixture. Therefore, the suitable temperature to investigate was 60^{o}C.

3.3.2 Influence of molar ratio H_2O_2/C=C on conversion of C=C bond

Epoxidation was carried out at 60^{o}C, 500 rpm, molar ratio of CH_3COOH/C=C 1:1 in 4 h. Molar ratios of H_2O_2/ C=C were varied to 1:1, 1:2 and 3:1. The iodine value of obtained products were measured and presented in Table 6.

Table 6: Iodine value of epoxidized produced at different molar ratio of H_2O_2/C=C

Molar ratio H_2O_2/ C=C	Iodine index (g I_2/100g)
1:1	52.6
2:1	43.3
3:1	31.2

As seen in the table, when molar ratio H_2O_2/C=C increased from 1:1 to 3:1, iodine value decreased correspondly from 56.2 to 31.2. This change is reasonable since more H_2O_2 will shift equilibrium of its reaction with CH_3COOH to form more CH_3COOOH that is the reactant in epoxidation step. At molar ratio H_2O_2/C=C of 3:1, temperature of 60°C, conversion of C=C bond in the original blend was 75.93%.

The molar ratio of H_2O_2/C=C is limited to 3:1 to ensure that the reaction takes place safely because of strongly oxidising character of H_2O_2 and strongly exothermic reaction.

3.3.3 Influence of reaction time on conversion of C=C bond

The epoxidation was proceeded at suitable temperature and molar ratio H_2O_2/C=C in the conditions described in the previous part and time of reaction was varied between 4 and 7 h. The results were recorded in Table 7.

Table 7: Iodine value of epoxidized produced at different time of reaction

Reaction time (h)	Iodine index (g I_2/100g)
4	31.2
5	9.9
7	6.9

The conversion of C=C bond went up significantly from 75.93% to 92.36% if the time extended from 4 to 5 h. Following that, it increased slowly by 2.32% when the reaction carried out more 2 h. Therefore, the time of reaction plays an important role in the epoxidation and it may be investigated to 10 or 20 h until the reaction occurs completely.

3.4 Oxirane ring opening

As investigated, the mixture of refined sunflower and soybean oil with mass ratio of 80:20 which suffered epoxidation at 60°C, molar ratio of H_2O_2/C=Cof 3:1, reaction time of 7 h has improved viscosity index and especially iodine value. However, viscosity value of this product is still slow and needs to be increased in some applications.

Thus, oxirane ring opening of the epoxidized product was carried out with expectation to boost viscosity values. In this reaction, n-butanol was selected to be agent because of its suitability structure. Viscosity values of ring-opened product are measured and showed in Table 8.

Table 8: Viscosity value of final product after oxirane ring-opening reaction

Viscosity at 40°C	**48.40**
Viscosity at 100°C	9.67
Viscosity index	190.88

The result showed that the viscosity of final product was higher than original blended vegetable oil. However, the viscosity index went down to 190.88 compared with 235.71 of the blend of vegetable oils. In addition, the pour point of ring-open product was 5°C being lower than original blend oil (7°C).

After blending, the obtained oil had equal quality with the base stock SN150, but there were limitations in its thermo-oxidative stability and its high pour point. After the modification in the structure, the viscosity of oil was similar with mineral oil SN250, the iodine value decreased effectively, the pour point reduced but still high. Therefore, this pour point is expected to be improved by adding pour point depressant additive in manufacturing lubricants.

4 CONCLUSIONS

Blending oil is a simple method to make vegetable oil become more applicable as a base oil in lubricant. Compared to pure vegetable oil, the blend of refined sun flower oil with soybean oil of 80:20 (mass ratio) was the best blended one among others. This mixture had the highest VI value of 235.71, suitable acidic and saponification values. However, there was still the presence of much C=C bond in the molecular chain. The results indicated that by changing the reaction condition in epoxidation and oxirane ring-opening reaction, the iodine value of the blend oil could be improved effectively. At 60°C, molar ratio H_2O_2/C=C of 3:1, reaction time of 7 h, molar ratio CH_3COOH/C=Cof 1:1 with 30 ml of CH_3COOH, stirring speed of 500 rpm, the epoxidized product had iodine value of 6.9 compared to the original blend oil of 129.6. This indicated that the resistance to oxidation of epoxidized blended vegetable oil is improved significantly.

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