

OXIDATION STABILITY OF CASTOR OIL IN SOLVENT EXTRACTION

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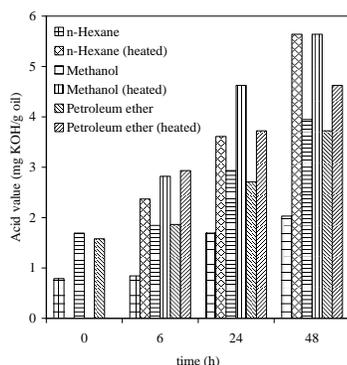
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Graphical abstract



Abstract

The present work aims to investigate the oxidation stability of castor oil obtained via three solvents, namely n-hexane, methanol and petroleum ether. Oxidation test was performed at ambient temperature and 120°C, and the oil was characterized according to its viscosity and acid value at different time intervals. Results show that the n-hexane extract is low in acid value, and exhibits good oxidation stability at ambient condition. For all oil extracts, heating at higher temperature accelerates the oxidation, thus increasing the viscosity and acid value. This behaviour is more pronounced for methanol extract. Although methanol and petroleum ether extracts possess high acid value, the latter reveals a better oxidation resistance at longer heating period compared to the former.

Keywords: Acid value, castor oil, oxidation stability, viscosity

Abstrak

Kajian ini bertujuan mengenalpasti kestabilan pengoksidaan minyak kastor diperolehi dengan tiga pelarut, iaitu n-heksana, metanol dan petroleum eter. Ujian pengoksidaan dijalankan pada suhu persekitaran dan 120°C, dan minyak dicirikan mengikut kelikatan dan nilai asid pada selang masa berbeza. Keputusan menunjukkan ekstrak n-heksana mempunyai nilai asid rendah, dan mempamerkan kestabilan pengoksidaan yang baik pada keadaan persekitaran. Untuk semua ekstrak minyak, pemanasan pada suhu lebih tinggi mempercepatkan pengoksidaan, justeru meningkatkan kelikatan dan nilai asid. Sifat ini lebih ketara bagi ekstrak metanol. Walaupun ekstrak metanol dan petroleum eter mempunyai nilai asid yang tinggi, ekstrak petroleum eter memberikan rintangan lebih baik terhadap pengoksidaan pada tempoh pemanasan lebih lama berbanding ekstrak metanol.

Kata kunci: Kelikatan, kestabilan pengoksidaan, minyak kastor, nilai asid

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1.0 INTRODUCTION

Lubricants mostly used nowadays are obtained from petroleum based derivative, i.e., mineral oil from de-waxed paraffin-based crude oil. The use of mineral oil is driven by its good characteristics and low price [1]. However, mineral oil is persistent and toxic to living organisms and marine creatures [2]. About 80% of lubricants finding their way into the environment and

water reservoir through leaks, spills, line breakage and fitting failure [3]. Due to its poor biodegradability, mineral oil thus becomes a major source for long-term pollution to the environment.

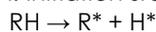
The shift to bio- or vegetable-based lubricant has now become a subject of considerable interest due to increasing concern over environmentally friendly lubricant that is renewable and biodegradable[4-6]. Vegetable sources such as palm oil [7], soy bean [8],

Jatropha seed [9-10] and castor bean [11-13] are among the promising candidates of bio-lubricant. It has been reported that vegetable-based oils possess comparable or even better technical properties than the mineral oil [14]. Yet, criticisms may arise from the use of edible vegetable oil as lubricant due to food security and possible disturbance in the supply of food chain. Thus, selection of naturally growing and non-edible vegetable is a better solution for potential source of bio-lubricant [12]. One of the promising candidates under this category is castor bean [15].

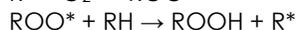
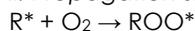
Castor bean with botanical name of *Ricinus communis* L is a semi-woody large shrub green herbaceous. It is originated from Middle East and North Africa, and widely grown in tropical areas. Castor oil is one of few naturally high purity glycerides that contains nearly 90% of hydroxyl fatty acid namely ricinoleic acid (molecular formula, $C_{18}H_{34}O_3$ structurally known as cis-12-hydroxyoctadeca-9-enoic acid) [11]. It gives high acetyl or hydroxyl value, and comparable iodine value [12-13]. Like other vegetable oils, castor oil exhibits oxidation that changes its physicochemical properties [8].

Oxidation readily occurs within the oil components and has obvious impacts in shelf-life, thus limiting its applications [16]. It is mainly driven by various factors such as air exposure, temperature, moisture, light and foreign matters. Oxidation is a process of complex reaction whereby the oil molecules are breaking down into smaller chains, and the new formed compounds would increase insoluble matter and oil acidity [17]. The oxidation mechanism encompasses initiation, propagation, branching and termination.

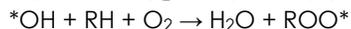
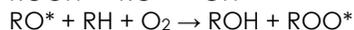
i. Initiation stage



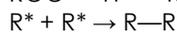
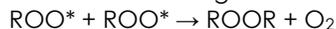
ii. Propagation stage



iii. Branching stage



iv. Termination stage



Oxidation is initiated by departing of proton from α -methanilic carbon to unsaturated bond of glyceride molecule, and forming free radicals [17-18]. The free radical attack oxygen to form unstable peroxy free radical (ROO^*). Lipid molecule is attacked by peroxy free radical to form hydroperoxide ($ROOH$) and another free radical, thus propagating the oxidation process. Branching stage is described by breaking down of hydroperoxide into more free radicals that trigger auto oxidation of unsaturated bonds. Primary oxidation compound, namely hydroperoxide was reported to increase the wear of engine parts that utilize mineral oil lubricant [18].

Physicochemical properties of castor oil have been widely documented [11-13]. However, information

regarding its oxidation stability is not adequately addressed in much of published literature. Therefore, this present study aims to establish the profile of oxidation stability of castor oil in solvent extraction. Effect of solvents and changes observed in viscosity and acid value are discussed.

2.0 EXPERIMENTAL

2.1 Materials

Castor bean was purchased from Ancient Greenfield PL, India. All solvents used (n-hexane, methanol and petroleum ether) are of analytical grade, and were manufactured by R&M chemicals, United Kingdom.

2.2 Oil Extraction

Castor seed was ground using pestle and mortar, and dried in oven at 60°C for 24h. The dried seed was ground again using blender to achieve uniform particle size. The castor oil was obtained via Soxhlet extraction.

About 50g of seed was placed in thimble, and 300mL solvent was poured into round bottom flask. The solvent was heated to its boiling point, and the experiment was allowed to run for 6h. The oil was separated from solvent using vacuum rotary evaporator. The oil was then placed in oven at 60°C for 24h until the weight is constant. Same procedures were repeated to obtain sufficient volume of oil by different solvents for analysis. The yield was calculated as weight of oil over weight of dry seed.

2.3 Viscosity and Density of Castor Oil

Viscosity of castor oil was determined by rheometer (Brookfield Programmable Rheometer, Model DV-III). Density of oil was calculated as weight of oil in 10mL density cup over volume of the cup.

2.4 Oxidation Stability of Oil

Oxidation stability of oil was determined using accelerated oxidation process [16, 19]. Briefly, different batches of oil in glass container were placed in oven at 120°C . At different time intervals, the glass container was taken out and the oil was analyzed for viscosity and acid value. Control setting was also employed at ambient temperature for comparison.

Acid value is the proportion of free fatty acid present in oil. It is defined as the amount of 0.1M KOH (in mg) needed to neutralize acid in 1g of oil. Five grams of oil was mixed with 50mL of diethyl ether-ethanol (50% v/v) mixture in 250mL conical flask. The mixture was heated using hot plate for 10min. Then, few drops of phenolphthalein indicator were added into the mixture. After which, potassium hydroxide solution was added slowly into the mixture. Titration was stopped when dark pink color which indicates

the neutralization end point appeared. Free fatty acid was calculated as,

$$\text{Free fatty acid (FFA, \%)} = \frac{\text{mL of KOH} \times 0.1 \times 28.2}{\text{weight of oil sample}} \quad (1)$$

where acid value is determined as $2 \times \text{FFA}$.

3.0 RESULTS AND DISCUSSION

3.1 Oil by Solvent Extraction

Table 1 shows the yield and density of castor oil extracted by n-hexane, methanol and petroleum ether. In general, n-hexane demonstrates a better extraction ability with 50% yield, while methanol displays a relatively lower yield of 44%. The colour of oil is pale yellow except for the one extracted using methanol. One possible reason for the reddish oil colour with tiny dark precipitates may suggest the unwanted transesterification when the oil was extracted in methanol although the temperature at which the extraction occurred was still low, and in the absence of catalyst [20]. Another possibility is the unexpectedly high pigmentation caused by field damage, improper storage, or faulty handling during crushing, extraction, or rendering. It is noteworthy that in the presence of oxygen, the amount of the carbon chain unsaturated fatty acids is a determinant factor for increased formation of alkyl radicals that react with oxygen, which impacted on the colour [22]. The values of oil density are almost comparable at 0.95g/cm^3 .

Table 1 Yield and density of castor oil by different solvents

| Solvent | Colour | Yield (%) | Density (g/cm^3) |
|-----------------|-------------|-----------|-----------------------------|
| n-Hexane | Pale yellow | 50.0 | 0.950 |
| Methanol | Reddish | 44.2 | 0.944 |
| Petroleum ether | Pale yellow | 47.6 | 0.944 |

3.2 Viscosity Profile of Castor Oil

Viscosity is an important property of lubricant [21]. It is defined as the ability of fluid to resist motion, and prevent wearing and heat generation as solid metals moved in different direction. Figure 1 illustrates the viscosity profile of castor oil at different spindle rotation speeds. In general, oil extracted using n-hexane shows a higher viscosity than the ones extracted using methanol and petroleum ether. The viscosity of each extract was found to increase with increasing spindle speed at increment ca. 200cP, confirming its nature as Newtonian fluid [21].

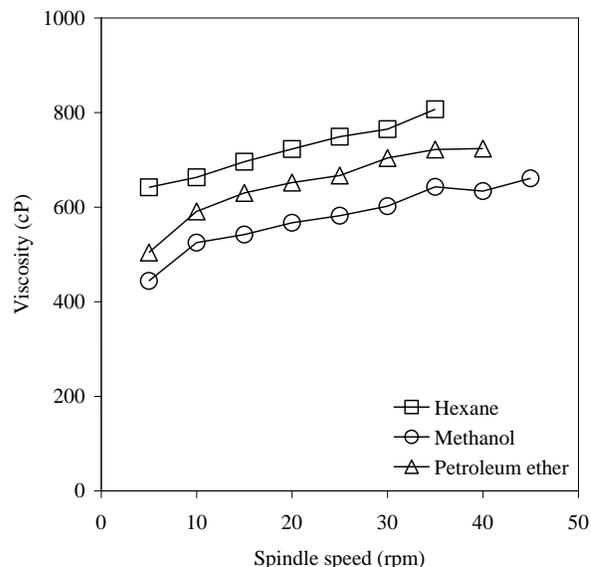


Figure 1 Viscosity profile of castor oil by different solvents

Figure 2 shows the viscosity profile against oxidation time for different oil extracts. The fluctuation in viscosity of oil extracts at elevated temperature of 120°C indicates the progress of oxidation process. All oil extracts that were heated for 6h exhibit a viscosity decrease at lower spindle speed of 20 rpm, thereafter gradually increased approaching viscosity at initial condition ($t=0\text{h}$) as the spindle speed increases. Similar pattern of viscosity for all oil extracts at this heating period could be interpreted as state of propagation in oxidation mechanism. The molecules of carboxylic acid byproducts formed in propagation state are likely to be the reason behind this phenomenon, and they are expected to give trivial increase in oil viscosity [18].

After 24h heating, all oil extracts demonstrate an increase in viscosity of more than 800cP which indicates a dramatic change in the composition of oil. Increment in oil viscosity at elevated temperature is an indication of oxidation, and such increase would result in excess energy consumption to overcome fluid friction and heat generation in lubricating applications [7]. Further heating for 48h results in no apparent viscosity difference, except for methanol oil extract where there is a slight increase of 40cP. It is believed that the degradation of oil has occurred at some point within 24h, and the branching stage at molecular level has been completed.

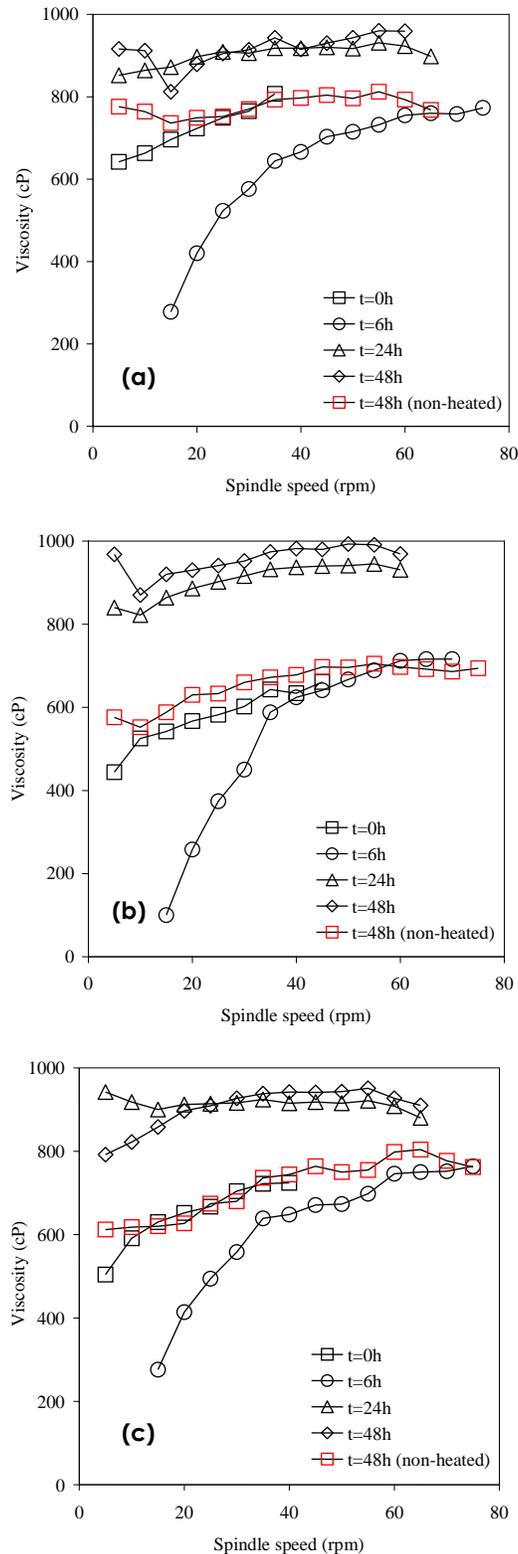


Figure 2 Effect of oxidation time on viscosity of castor oil extracted by (a) n-hexane, (b) methanol and (c) petroleum ether

At this stage, the number of carboxylic compounds are dramatically increased, and

consequently altered the oil ability to handle physical load.

According to the oxidative cleaving of hydrocarbon chains, the increase in oil viscosity is due to the strained interaction of non-homogeneous, higher and lower molecular weight compounds, and the decrease in the level of unsaturated fatty acids within the system, resulted from the termination stage [18]. Also, high molecular cyclisation and polymerization at high temperature mostly lead to undesirable formation of deposits and lacquers that increase the viscosity and decrease the performance of lubricant [20-21].

In contrast, the control oil samples left after 48h reveal nearly the same and unchanged pattern of viscosity as the initial samples ($t=0h$). It implies that the oil content is relatively stable under ambient temperature. Notwithstanding that, oil is believed to undergo some oxidation but the effect is quite small, and it is barely at the initiation stage. In these control samples, the driving force for oxidation is limited to the exposure with surrounding air, and it is not as critical as heat (at $120^{\circ}C$) in promoting the chains breaking [16].

3.3 Acid Value Profile of Castor Oil

The presence of free fatty acid compounds in oxidation increases the oil acidity [17]. Therefore, acid level is used to evaluate the progress of oil oxidation. Figure 3 displays the acid value of castor oil at the beginning of oxidation under heated condition (oven, $120^{\circ}C$). Oil extracted using n-hexane exhibits a smaller acid value of $0.79mg$ KOH/g, which is about twice as lower as that of methanol and petroleum ether oil extracts. The low acid value would favor n-hexane to be used as solvent in oil extraction. It infers that methanol and petroleum ether could promote oil oxidation during the course of solvent extraction. The increase of acid value with increasing the period of heating signifies the occurrence of oxidation in all oil samples.

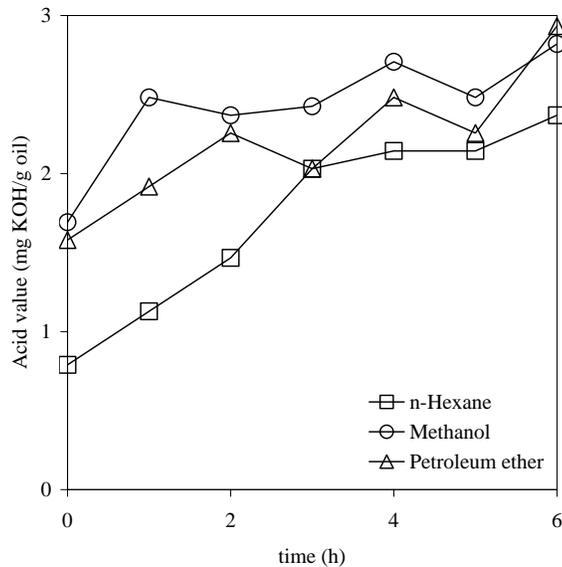


Figure 3 Acid value of castor oil at initial period of heated oxidation

Acid values for methanol and petroleum ether oil extracts are surpassed the recommended value of 1mg KOH/g. In lubricant and high pressing environment, the acid value should not be allowed to increase more than +0.5 higher than that of new oil, while for most mineral lubricant, acid value that exceeds 4mg KOH/g is considered corrosive [18]. From Figure 3, n-hexane oil extract reaches the alert level of 2mg KOH/g oil sometime after 2h of induction time, and reaches the alarming level of 2.14mg KOH/g oil when single unit increment was recorded after 4h. On the other hand, petroleum ether oil extract demonstrates a better oxidation resistance as the alerting value of 2mg KOH/g oil was observed only after 3h heating in oven, while methanol oil extract shows poor oxidation resistance as the value reaches 2.48mg KOH/g oil within only 1h.

Figure 4 shows the profile of acid value for heated and non-heated oil samples at different time intervals. Both heated and non-heated samples demonstrate a common rising trend of acid value as the time elapsed. However, heated samples show a higher acid value than the non-heated ones, showing that the oxidation is accelerated under heating. Increase in acid level was possibly due to activation of fat-reducing enzymes by moisture, and hydrolysis of the oils is initiated, the water then hydrolyze the fatty acids from the triglycerides, releasing free fatty acid and consequently increasing the acid value.

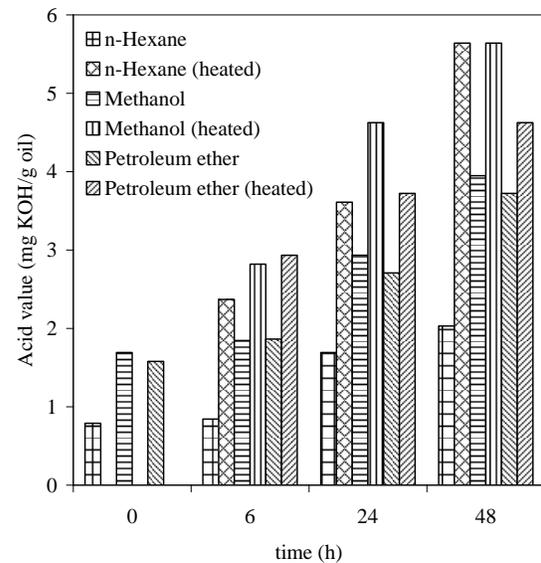


Figure 4 Acid value of castor oil under heated and non-heated oxidation

The acid value for heated n-hexane oil extract reaches 3.6mg KOH/g after 24h, and elevates beyond the corrosive limit after 48h at which the oil is assumed to be degraded. On the contrary, the heated methanol oil extract is already corrosive within 24h. At such high acid value, castor oil may introduce poor lubricating performance and considered as corrosive. When compared to the former two oil extracts, the heated petroleum ether oil extract requires longer period to exceed the corrosive limit of 4.62mg KOH/g. This again explains the resistance to oxidation of the oil extracted using petroleum ether.

4.0 CONCLUSION

Castor oil was obtained by extraction using three different solvents, and the profiles of oxidation stability for each extract are established. Oil with high yield and low acid value was extracted using n-hexane. It demonstrates good oxidation stability under ambient temperature, and becomes corrosive only after 48h heating at 120°C. Oxidation of methanol oil extract was accelerated as a function of time at elevated temperature. High acid value was initially recorded for methanol and petroleum ether oil extracts. However, the latter exhibits a better oxidation resistance at longer heating period compared to the former.

Acknowledgement

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