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Effect of Temperature on Corrosion Behavior of Metals in Rubber Seed Oil

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Nine types of metal including bonderized iron, iron, black scale, mild steel, copper, brass, aluminum, SUS 304 and SUS 316 were immersed in rubber seed oil (RSO) at 303, 318 and 328 K to investigate the corrosion behavior of the metals in this oil. Cooking palm oil (CPO) was used as a reference, which contains a lower concentration of free fatty acids (FFA) than RSO. The acid values (AV) of the RSO and CPO were 91.4 and 0.23 mg-KOH/g, respectively. The metals used in this study showed constant corrosion rates in RSO throughout the time period of the corrosion test (28 d). The following order for the corrosion rate was observed: mild steel>iron=bonderized iron = black scale > brass = copper > SUS304 = SUS316 = aluminum. SUS304, SUS316 and aluminum exhibited no substantial corrosion in RSO. The activation energy for the corrosion rate was calculated for iron, mild steel, copper and brass to be 61.4, 46.9, 29.0 and 23.2 kJ/mol, respectively. The corrosion rate of all the metals in CPO was substantially zero at 318 and 328 K.

Key Words

Rubber seed oil, Palm oil, Metal, Corrosion rate, Activation energy, SEM

1. Introduction

Fatty acid methyl ester (FAME) is a replacement for fossil fuel diesel oil. Use of FAME as a replacement of diesel fuel can mitigate fossil fuel depletion and green house gas emission. From the reaction engineering view point, some developed reaction technologies have been reported^{1)~4)}. From the feedstock view point, we need to use non-edible oils to avoid the food-energy issue. Rubber seed oil (RSO) is one of the non-edible oils available in ASEAN countries including Malaysia⁵⁾. RSO is therefore a good candidate for raw material for the production of FAME type biodiesel. For production, transportation and storage of this oil, it is important to know the corrosion behavior of representative metals in this oil. The authors could not find any study for corrosion of metals in RSO.

In the present study, nine types of metal including bonderized iron, iron, black scale, mild steel, copper, brass, aluminum, SUS 304 and SUS 316 were immersed in RSO and cooking palm oil (CPO) at 303, 318 and 328 K to investigate the corrosion behavior of the metals in these two oils. CPO was specifically used as a reference, which con-

tains smaller amount of free fatty acids (FFA) than RSO.

2. Experimental

2.1 Material

The rubber seed oil (RSO) used in this study was purchased from Kinetics Chemicals (M) Sdn Bhd in Malaysia, who imported the oil from Vietnam. The cooking palm oil (CPO) was purchased at a local market place. The acid values (AV) of the RSO and CPO were 91.4 and 0.23 mg-KOH/g, respectively. These feedstocks were kept in a refrigerator maintained at a temperature below 278 K, and utilized in this experimental work without any further pretreatment.

Table 1 shows the physicochemical properties of RSO used in this study. The density was measured at 293 K by a density meter (DMA4500, Anton Paar). The viscosity was measured at 313 K by a rotating cylinder type viscosity meter (CAP2000, Brookfield). The moisture content was measured by a Karl-Fischer titrator (V30, Mettler Toledo). The iodine and acid values were measured according to AOC1977 and EN14104, respectively. The fatty acid composition in FFA part was measured as follows. The FFA in RSO was esterified with methanol by H₂SO₄ catalyst. The molar ratio of methanol to RSO was 12:1. The catalyst concentration (RSO basis) was 12 wt%. The esterification was conducted at 333 K for 90 min in a three-necked round

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Table 1 Physicochemical properties of rubber seed oil

Physicochemical properties		
Density [kg/m³] at 293 K	918	
Viscosity [mPa · s] at 313 K	24.4	
Moisture content [mg/L]	2658	
Iodine value [g-I ₂ /100g]	146	
Acid value [mg-KOH/g]	91.4	
Fatty acid composition		
Acid type	Acid in FFA part of RSO [wt%]	Acid in entire RSO [wt%]
Myristic (C14:0)	0.11	0.08
Palmitic (C16:0)	8.93	8.84
Palmitoleic (C16:1)	0.25	0.19
Stearic (18:0)	6.91	8.10
Oleic (C18:1)	25.13	25.08
Linoleic (C18:2)	41.14	40.40
Linolenic (C18:3)	16.64	16.49
Arachidic (C20:0)	0.31	0.35
Behenic (C22:0)	0.15	0.19
Erucic (C22:1)	0.13	0.11
Lignoceric (C24:0)	0.30	0.17

bottom Pyrex flask. The mixture was injected into a GC-FID (Shimadzu GC2010 with capillary column BPS70). The fatty acid concentration was approximated by the GC area percentage of FAME obtained. The reaction mixture obtained above was further transesterified with methanol by KOH catalyst. The molar ratio of methanol to RSO was 10:1. The catalyst concentration (RSO basis) was 2 wt%. The esterification was conducted at 333 K for 60 min in a three-necked round bottom Pyrex flask. The mixture was injected into the GC-FID. The fatty acid concentration was approximated by the GC area percentage of FAME obtained. The smallest fatty acid detected in either FFA part or entire RSO was methyl myristate. Formate, acetate and propionate were not detected.

Metal test pieces used in this study were purchased from a local supplier in Malaysia and a material supplier in

Japan. They include bonderized iron, iron, black scale, mild steel, aluminum, brass, copper, SUS304 stainless steel and SUS316 stainless steel. Their shape is a plate of 10 mm in length and 10 mm in width. They are listed in **Table 2**. Before corrosion test, metal test pieces without coatings were polished by a #3000 sand paper, and then cleaned by acetone. Metal test pieces with coating, *i. e.*, bonderized iron and black scale, were only cleaned by acetone.

2.2 Corrosion experiment

The RSO was poured into a glass tube with a plastic screw cap. Each test piece was then placed into the glass tube. The glass tubes containing RSO and test piece were placed in a hot water bath at 303, 318 and 328 K. At certain time intervals between 1 and 2 weeks, each metal sample was taken from the glass tube. Then it was cleaned with tetrahydrofuran, and was wiped. After it was weighed and visually inspected, it was returned to the glass tube. The corrosion test was carried out for 28 d.

Another series of corrosion test was carried out by using the CPO and the same types of metal at 318 and 328 K.

Specific types of metal were observed before and after the corrosion test by a scanning electron micrograph (Carl Zeiss Supra 55VP FESEM).

3. Results and discussion

3.1 Corrosion rate of metals in RSO and CPO

The mass loss of each metal test piece was plotted against the immersion time in RSO. **Figs. 1, 2 and 3** show the results at 303, 318 and 328 K, respectively. On the other hand, metals immersed in CPO did not show substantial mass loss throughout the test time period at 318 and 328 K. The trend of mass loss in RSO against the immersion time can be approximated by a straight line as shown in the three figures. This fact exhibits that the corroded surface of each metal has maintained the same reactivity with the RSO throughout the time period of the corrosion test.

Fig. 4 shows the corrosion rate of the metals in RSO

Table 2 Metal test pieces used in this study

Metal	Thickness [mm]	Length [mm]	Width [mm]	Remark
Bonderized iron	0.5	10	10	Iron with zinc layer
Iron	0.5	10	10	Zinc layer removed bonderized iron
Black scale	1	10	10	Mild steel with black oxide layer
Mild Steel	1	10	10	Oxide layer removed black scale
Copper	1	10	10	-
Brass	1	10	10	-
Aluminum	1	10	10	-
SUS304	1	10	10	-
SUS316	1.5	10	10	-

Fig. 1 Mass loss of metals against immersion time in rubber seed oil at 303 K

Fig. 2 Mass loss of metals against immersion time in rubber seed oil at 318 K

Fig. 3 Mass loss of metals against immersion time in rubber seed oil at 328 K

plotted against the temperature. The corrosion rate R_c was calculated from the mass loss slope in Figs. 1 to 3 by using the following equation:

$$R_c = \frac{\Delta m}{\Delta t} \frac{10^3}{24 \times 3600} \frac{1}{S_m} \quad (1)$$

where R_c denotes the corrosion rate in [$\mu\text{g}/(\text{m}^2 \cdot \text{s})$], Δm the mass loss in [mg], Δt the immersion time in [d], S_m the external surface area of metal piece [m^2].

Fig. 4 Corrosion rate of metals in rubber seed oil as a function of temperature

The metals used in this study showed the following corrosion rate order: mild steel > iron = bonderized iron = black scale > brass = copper > SUS304 = SUS316 = aluminum. SUS304, SUS316 and aluminum exhibited no substantial corrosion in RSO. It is very likely that free fatty acids in the RSO caused the corrosion since the metals showed no substantial corrosion in the CPO used in the present study, which does contain quite lower concentration of free fatty acids than the RSO (see Table 1). Since the RSO contains 2.7 g/L of water as listed in Table 1, proton formation from the free fatty acids is thought to be possible. It is worthwhile to mention that the order of the corrosion intensity mentioned above is not perfectly consistent with the order of the ionization tendency; $\text{Al} \succ \text{Fe} \succ \text{H} \succ \text{Cu}$. According to this tendency, aluminum must be corroded more than iron, and copper must not be corroded. In fact aluminum was not corroded, and copper was corroded in the present study. Aluminum is known to form a very fine corrosion-resistant oxide layer on its external surface⁶⁾. The protective effect from the fine layer formed on aluminum may be the reason of what was observed in the present study. Although the fact that copper was corroded by RSO in this study cannot be well explained from the ionization tendency, a previous study reported a similar result⁷⁾.

The corrosion rates of irons, aluminum and brass in RSO were compared with previous papers. The results are summarized in Table 3. Sugimoto reported the corrosion rate of iron to be 2×10^2 to $9 \times 10^3 \mu\text{g}/(\text{m}^2 \cdot \text{s})$ at 298 K in 0.5M H_2SO_4 ⁸⁾, which is quite higher than that of irons at 303 K in the present study. This higher corrosion rate in the literature may be attributed to a higher proton concentration in the H_2SO_4 than that in the RSO. Sato reported the corrosion rate of aluminum to be $5 \times 10^2 \mu\text{g}/(\text{m}^2 \cdot \text{s})$ in H_2SO_4 (pH=1) at room temperature⁹⁾, whereas there was no substantial corrosion in the present study due to a pro-

Table 3 Comparison of corrosion rate of this study with previous studies

Metal	Corrosion rate [$\mu\text{g}/(\text{m}^2 \cdot \text{s})$] in this study	Corrosion rate [$\mu\text{g}/(\text{m}^2 \cdot \text{s})$] in literature
Irons	2 to 5 at 303 K	2×10^2 to 9×10^3 at 298 K in 0.5M H_2SO_4 ⁸⁾
Aluminum	Substantially zero at 303 K	5×10^2 in H_2SO_4 (pH=1) at room temp ⁹⁾
Brass	0.76 at 328 K	20 in oleic acid/benzyl alcohol (1:4 in volume) at 333 K ¹⁰⁾

protective layer formation. This difference may be attributed to the difference of acid type between the present and previous studies. Notoya reported the corrosion rate of brass be $20 \mu\text{g}/(\text{m}^2 \cdot \text{s})$ in oleic acid/benzyl alcohol (1:4 in volume) at 333 K¹⁰⁾, which is higher than that of brass at 328 K in the present study. This discrepancy may be from the higher concentration of oleic acid and the higher temperature in the previous study.

3.2 Activation energy of corrosion rate in RSO

The activation energy was obtained by the Arrhenius plot (Fig. 5) using the results shown in Fig. 4. The values of activation energy are summarized in Table 4 together with the values previously reported^{11) 12)}. The activation energy of the four metals obtained in this study ranges from 20 to 60 kJ/mol, which implies that the reaction rate observed was not controlled by mass transfer.

3.3 Surface observation of metals before and after corrosion in RSO

Fig. 6 shows SEM photographs of SUS304, mild steel, copper and brass before and after the corrosion test. The external surface of SUS304 showed no change as can be seen from Fig. 6(a). On the contrary, mild steel, copper and brass showed a change of surface morphology after the corrosion test. These trends observed by SEM are consis-

Fig. 5 Arrhenius plot

tent with the results from mass loss shown in Fig. 4.

4. Conclusion

In the present study, nine types of metal including bonderized iron, iron, black scale, mild steel, copper, brass, aluminum, SUS 304 and SUS 316 were immersed in rubber seed oil (RSO) and cooking palm oil (CPO) at 303, 318

Fig. 6 SEM photographs of metal surface before and after the corrosion experiment in rubber seed oil at 328 K

Table 4 Activation energy of corrosion rate

Metal	Activation energy of corrosion rate [kJ/mol] in this study	Activation energy of corrosion rate [kJ/mol] in literature	
Iron	61.4	NA	
Mild steel	46.9	41-49	In phosphoric acid, 0.5-2.0 M ¹¹⁾
Copper	29.0	NA	
Brass	23.2	18-24	In HCl, 3.4 % ¹²⁾

and 328 K to investigate the corrosion behavior of the metals in these two oils.

At all the three temperatures, iron, mild steel, brass and copper were corroded by RSO, whereas CPO did not substantially corrode any of them. From the comparison of the results between RSO and CPO, corrosion of metals by RSO may be attributed to the free fatty acid existing in RSO. From the corrosion experiment results using RSO, SUS 304, SUS 316 and aluminum are recommended to use as the material for storage, transportation and reaction vessels.

The corrosion rates observed may have not been controlled by mass transfer.

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