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Physicochemical Characteristics of Fumarized and Maleinized Cottonseed Oil

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ABSTRACT

Cottonseed oil, an example of a renewable resource was treated with different amounts of 2% ($MACOSO_1$), 5% ($MACOSO_2$), 10% ($MACOSO_3$) and 15% ($MACOSO_4$) of maleic anhydride, and 2% ($FUCOSO_1$), 5% ($FUCOSO_2$), 10% ($FUCOSO_3$), and 15% ($FUCOSO_4$) of fumaric acid. The physicochemical properties of the maleinized and fumarized cottonseed oil samples were evaluated and compared with the pure cottonseed oil. The acid and saponification values of maleinized and fumarized samples were greater than that of cottonseed oil. The colour of fumarized samples were yellow-brown and were brighter than the colour of cottonseed oil, which was brown. The iodine value of both maleinized and fumarized samples decreases and were lower than that of cottonseed oil. The percentage double bonds used up was greater in maleinization than in fumarization of cottonseed oil. The lower volatile organic component of both maleinized and fumarized samples implies that they could be a better monomer for synthesis of eco-friendly polymer.

KEY WORDS: *Acid value, Cottonseed oil, Fumarization, Iodine value, Maleinization*

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I. INTRODUCTION

The fatty acid esters derived from the triglyceride vegetable oils are an attractive source of raw materials for polymer and composite materials synthesis [1 and 2]. Various vegetable oil sources that are used for preparation of biopolymers (alkyd resins) are tall, soybean, cottonseed, melon seed, rubber seed, tobacco seed oils [3, 4, 5, 6, 7, 8 and 9] and many others. A common property of these oils is their high degree of unsaturation. Natural oils that can be derived from both plant and animal sources are found in abundance in all parts of the country, making them an ideal alternative chemical feedstock. These oils have relatively low cost and environmentally benign properties. They contain active sites amendable to chemical reaction; these sites are the double bond, the allylic carbons, the ester group, and the carbons alpha to the ester group [2]. These active sites can be used to introduce polymerizable groups on the triglyceride using the same synthetic techniques that have been applied in the synthesis of petroleum – based polymers.

Previous work in our laboratory show that cottonseed oil contains two unsaturated fatty acids (octadec-9-enoic and octadec-9,12-dienoic acids) with octadec-9-enoic acid (75.56%) as the most abundant unsaturated fatty acid. The iodine value of the oil was determined as $100.251gI_2/100g$ and the oil was classified as semi-drying oil [3]. Due to environmental hazards associated with petroleum-based feedstock, increase in industrialization rate and population, it is envisaged that there will be a continuous increase in demand for eco-friendly feedstock for polymer synthesis. Hence, this research is aimed at modifying the properties of cottonseed oil through maleinization and fumarization of the oil thereby widening the scope of application of the oil as a precursor for synthesis of water-reducible coatings.

II. EXPERIMENTAL

2.1 Materials

Cottonseed oil (COSO) was purchased at Sabongari market, Kano and used for the maleinization and fumarization without further purification. Analytical grade maleic anhydride (MA), and fumaric acid (FA) were obtained from commercial sources and used in the maleinization and fumarization processes without further purification.

2.2 Maleinization and Fumarization of COSO

Maleinization and fumarization of COSO were carried out using the method described by [10] with slight modification. Four samples each of maleinized cottonseed oil (MACOSO) were prepared by heating

115.13g of COSO with 2%, 5%, 10% and 15% maleic anhydride (w/w) respectively under reflux at temperature between 200 and 230 ^{0}C for about 90 min in a 1 litre round bottom flask. Fumarization of COSO (FUCOSO) was also carried out using 2%, 5%, 10% and 15% fumaric acid and 115.13g of the oil based on the procedure described above. Lead (II) Oxide (PbO) was used as the catalyst for fumarization and maleinization processes respectively. The Calculated amount of maleic anhydride and fumaric acid used in the preparation of MACOSO and FUCOSO are indicated in the recipe, Table 1.

Maleinization and fumarization was believed to proceed via type I and II Diels – Alder reactions. The percentage double bonds used up during the processes were calculated using the relationship:

$$\% \text{ double bond used up} = \frac{IV\ of\ oil - IV\ of\ sample}{IV\ of\ oil} \times \frac{100}{1} \qquad (1)$$

where IV is the iodine value.

The reaction schemes and the expected structure of maleinized and fumarized products are shown in Figures 1 and 2.

2.3 Characterization of Maleinized and Fumarized Cottonseed Oil

The physicochemical properties viz: colour, specific gravity, acid value, iodine value, saponofication value, volatile and non-volatile matter of the maleinized and fumarized oils were determined using IUPAC standard method [11].

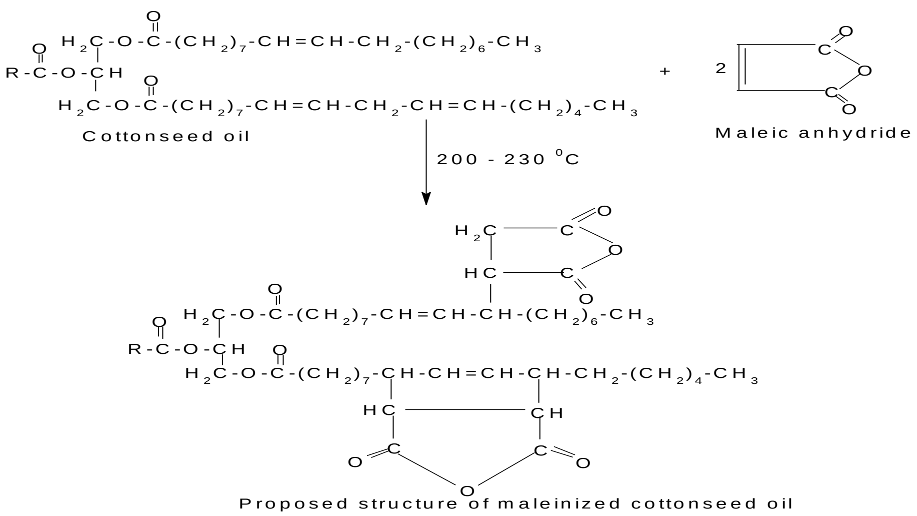

Figure 1: Proposed reaction scheme for the maleinization of cottonseed oil

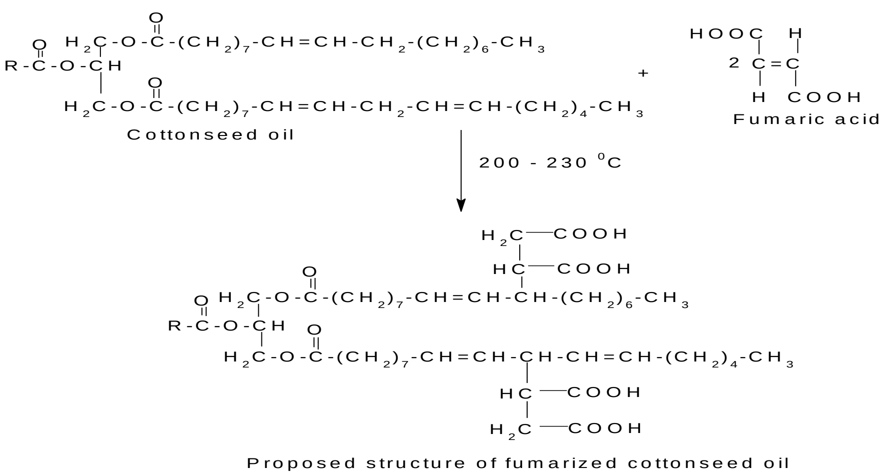

Figure 2: Proposed reaction scheme for the fumarization of cottonseed oil

III. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of FA Modified COSO

Table 2 shows the physicochemical properties of fumarized cottonseed oil. The samples of fumarized cottonseed oil were yellow – brown and were brighter in colour than cottonseed oil. Fumarization of the triglyceride oil seems to improve upon the physical appearance (colour) of the oil. Therefore, if used in preparation of alkyd resins, gloss and colour properties of the product will be better than that produced from the ordinary COSO.

The specific gravity of the fumarized oil ($FUCOSO_1$ – $FUCOSO_4$) increases as the percentage of fumaric acid increases and were slightly higher than that of COSO (Table 2). The slight difference in the specific gravity of fumarized oil and the cottonseed oil counterpart may be attributed to modification of cottonseed oil with fumaric acid. Saponification values of the FUCOSO samples increases with increase in the content of fumaric acid and are higher than that of cottonseed oil (Table 2). Similarly, acid values of FUCOSO samples increases with increase in the concentration of fumaric acid and are higher than the acid value of the cottonseed oil. The significant difference in the acid values between the fumarized samples and the triglyceride oil may be due to the high acid value of fumaric acid.

On the contrary, the iodine values of samples $FUCOSO_1$ – $FUCOSO_4$ are lower than the iodine value of COSO, and decreased with increase in the content of fumaric acid. This may be attributed to the fact that fumarization proceed via type II Diels – Alder reaction. The percentage of double bonds used up during fumarization of cottonseed oil was observed to increase from 2.67 – 14.26 % for $FUCOSO_1$ – $FUCOSO_4$ as the percentage of fumaric acid increases. Hence, it can be inferred that fumarization of COSO increases the level of acidity and decreases the unsaturation of COSO. The high percentage of non – volatile matter in the FUCOSO samples signifies that the fumarized samples will be very useful in producing eco-friendly resin.

3.2 Physicochemical Properties of MA Modified COSO

Table 3 shows the physicochemical properties of maleinized cottonseed oil. It is observed that the trends in properties of the MACOSO samples are similar to those of fumaric acid modified counterparts. The rate of loss of MA due to sublimation was greater than that of FA and increases as the percentage of MA in the samples increase. The acid values of MACOSO samples increased as the percentage of maleic anhydride increases. This observation may be due to high acid value of maleic anhydride. Guner *et al.* [12] and Aydin *et al*. [13] gave the acid value of MA as 1144.2 mgKOH/g. The colours of the maleinized triglyceride oil samples ($MACOSO_1$ – $MACOSO_4$) were brown as its COSO counterpart. Generally, the colours of MACOSO samples were brighter than the colour of COSO counterpart. Hence, the MA modified oil will produce alkyds with better gloss characteristics than the COSO alkyds. Similarly, the iodine values of $MACOSO_1$ – $MACOSO_4$ decreased as the percentage of MA increases and were generally lower than the iodine value of COSO (Table 3). This observation may be attributed to the possibility of the double bonds in the COSO, and MA being used up during the reaction, since it is believed that maleinization of cottonseed oil occurs through type I and II Diels – Alder reactions (see Figure 1). The percentage double bonds used up during maleinization of COSO was observed to increase from 40.03% **-** 44.46% for $MACOS_1$ – $MACOSO_4$ as the percentage of MA increases. The percentage double bonds used up during maleinization were greater than those of fumarization. This may be because only type II Diels – Alder reaction was taking place during fumarization, while both type I and II Diels – Alder reactions were occurring during maleinization (see Figures 1 and 2). Similar trend of results have been reported for maleinization of rubber seed oil [10]. Maleinization of triglyceride oils again increases the acidity and decreases the unsaturation of the oils. The percentage non – volatile components show that MACOSO samples can serve as a better raw material for production of water reducible alkyd resins, which are eco-friendly.

Table 1: Recipe for the maleinization and fumarization of cottonseed oil

	Parts by weight (g)		
Sample	COSO	Maleic anhydride (MA)	Fumaric acid (FA)
$MACOSO_1$	115.13	1.83	-
$MACOSO_2$	115.13	4.56	-
$MACOSO_3$	115.13	9.13	-
$MACOSO_4$	115.13	13.69	-
$FUCOSO_1$	115.13	-	1.83
$FUCOSO_2$	115.13	-	4.56
$FUCOSO_3$	115.13	-	9.13
$FUCOSO_4$	115.13	-	13.69

Table 2: Physicochemical properties of fumaric acid modified cottonseed oil

Properties		Fumaric acid modified cottonseed oil			
	COSO [3]	**FUCOSO$_1$**	**FUCOSO$_2$**	**FUCOSO$_3$**	**FUCOSO$_4$**
Colour	Light brown	Yellow-brown	Yellow-brown	Yellow-brown	Yellow-brown
Specific gravity (at 28^{0}C)	0.919	0.927	0.933	0.945	0.951
Acid value (mgKOH/g)	1.122	10.098	21.318	32.222	50.663
Saponification value (mgKOH/g)	189.338	235.620	256.658	280.500	291.720
Iodine value (gI_2/100g)	100.251	97.588	95.050	90.684	85.953
Non-volatile matter (%)	-	99.940	99.600	99.700	98.600
Volatile organic component (VOC) (%)	-	0.060	0.400	0.300	1.400

Table 3: Physicochemical properties of maleic anhydride modified cottonseed oil

Properties	Maleinized cottonseed oil				
	COSO [3]	**MACOSO$_1$**	**MACOSO$_2$**	**MACOSO$_3$**	**MACOSO$_4$**
Colour	Light brown	Brown	Brown	Brown	Brown
Specific gravity (at 28^{0}C)	0.919	0.917	0.926	0.943	0.962
Acid value (mgKOH/g)	1.122	15.361	24.034	39.967	51.175
Saponification value (mgKOH/g)	189.338	211.778	224.583	230.193	260.683
Iodine value (gI_2/100g)	100.251	60.126	58.857	58.222	55.684
Non-volatile matter (%)	-	96.303	92.708	92.080	90.930
Volatile organic component (VOC) (%)	-	3.697	7.292	7.920	9.070

IV. CONCLUSION

COSO was treated with different amounts of MA and FA respectively and their physicochemical properties determined. Incorporation of MA and FA into COSO increases the acid value and saponification value but decreases the iodine value. The percentage double bonds used up during maleinization was greater than that of fumarization and the MACOSO and FUCOSO samples were of lower volatile organic components. Hence, they could be useful in formulating eco-friendly coating. Fumarization of COSO followed Diels – Alder type I reaction while Maleinization followed Diels – Alder type I and II reactions.

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