

Studies on the Alcoholysis of Some Seed Oils

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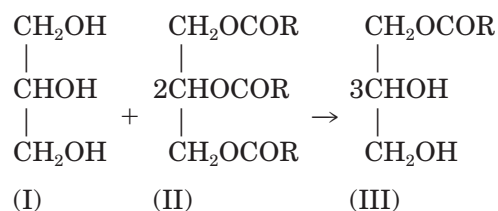
ABSTRACT: The effects of time and temperature on the alcoholysis of rubber seed, melon seed, linseed, and soyabean oils have been studied. The following temperatures were investigated: 200, 220, 245, and 260°C. Litharge (PbO) was used as the alcoholysis catalyst. The optimum alcoholysis temperature was found to be 245 ± 2 °C for each of the oils. At lower alcoholysis temperatures (<245°C), there is the preferential alcoholysis of seed oils derived from unsaturated acid; and the general alcoholysis rates were found to be in the following order: linseed oil \approx rubber seed oil \geq soyabean oil \approx melon seed oil. The alcohol-solubility of the oils is generally observed to begin at 42–45% conversion of oils to monoglycerides. The α -monoglyceride contents of the alcoholysis mixtures of rubber seed and linseed oils were generally similar at methanol tolerance, and higher than those of melon seed and soyabean oils. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1826–1832, 2000

Key words: alcoholysis; saturated acid; monoglyceride; methanol tolerance; alcohol-solubility

INTRODUCTION

In the surface coatings industry, the use of vegetable oils in the manufacture of oil-modified alkyd resins is enormous. These alkyd resins are the nonvolatile binders or vehicles in the production of oil paints and varnishes. The vegetable oils are incorporated into the alkyd structure by the alcoholysis reaction.

The alcoholysis of triglyceride oils is carried out to obtain partial esters best suited to produce linear polymers on subsequent polymerization. The alcoholysis of a vegetable oil is normally carried out with 2 mole of glycerol (I) for each mole of oil (II), since this ratio enables theoretically all the oils to be converted to monoglycerides (III):



where R = fatty acid radical. When pentaerythritol is used as the polyhydric alcohol (polyol), the fatty acid diester of pentaerythritol is the preferred product, and 1 mole of pentaerythritol per mole of oil is used.

Commercially, it is cheaper to produce alkyds from vegetable oils because these are normally cheaper than the equivalent quantity of fatty acid and glycerol.¹ However, in alkyd manufacture, attempts to react the vegetable oil, polyol, and dibasic acid usually lead to incompatibility because of the preferential reaction of the polyol and dibasic acid rather than with the oil.² To avoid this, alcoholysis of the oil is carried out prior to the esterification reaction. The progress of an al-

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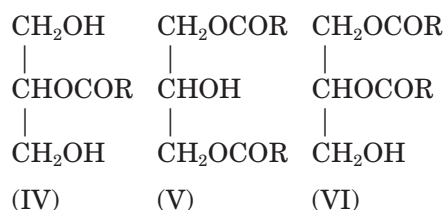
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Table I Fatty Acid Composition (%) and Iodine Values of Rubber and Melon Seed Oils

Oil Seeds	Oil Content (%)	Oleic	Linoleic	Linolenic	Saturated Fatty Acids	Iodine Values (mgI/g)
Rubber ^{6,7}	49	21.9	38.2	24.3	15.3	137.7
Melon ⁸	51	19	55.1	—	25.9	112.9

coholysis reaction is normally followed by measuring the solubility of the alcoholysis mixture in anhydrous methanol. The alcoholysis reaction is completed when 1 volume of the alcoholysis mixture is soluble in 2 volumes of anhydrous methanol.

The alcoholysis reaction does not go to completion under the conditions used in practice, and the alcoholysis product may be expected to contain α -monoglyceride (III), β -monoglyceride (IV), α, α' -diglyceride (V), α, β -diglyceride (VI), triglyceride or oil (II), and glycerol (1) when glycerol is used as the polyol. This mixture is referred to as a monoglyceride.



Because alcoholysis products are effective raw materials for alkyd resin manufacture, a knowledge of their composition becomes very important. This is with a view to reduce the batch to batch variations in properties of alkyd resins made from the same alcoholysis products and similar reaction conditions. Thus, Runk³ conducted alcoholysis of linseed oil with glycerol in the molar ratio 1 : 3 · 3 at 235°C in the presence of PbO. He found an α -monoglyceride content of 58–60% at equilibrium. The viscosities of alkyd resins of 52% oil length made from the alcoholysis mixtures were markedly dependent upon α -monoglyceride content. Pintile⁴ studied the alcoholysis of oils and found that the highest monoglyceride of final product was 54–55% and the lowest diglyceride content 23–24%. Sathyanarayana et al.⁵ carried out alcoholysis of linseed oil with glycerol under the same conditions as those for alkyd resin synthesis by the monoglyceride route. The partial glyceride formed in the alcoholysis reaction were characterized by TLC-FID (thin-layer chromatog-

raphy-flame ionization detector) and proton NMR (nuclear magnetic resonance). The predominant products they found were 1-monoglycerides, the concentration of which increased with the decrease in oil length. Of the isomeric diglycerides, the concentration of only 1,3-diglycerides varied but that of 1,2-diglycerides remained nearly the same in the formulations studied.

From the literature, the alcoholysis responses of the oils of melon and rubber seeds have not been reported. Melon and rubber seed oils are triglycerides, and are thus composed of the glycerides of fatty acids. Melon seed oil is light yellow in color whereas rubber seed oil is reddish-brown; both can be obtained from their oil-bearing seeds by solvent extractions. The chemical compositions of rubber and melon seed oils are shown in Table I. Rubber seed oil contains mostly linoleic and linolenic acids with small proportion of oleic acid and saturated fatty acids. The oil is a drying oil and is characterized by the property of absorbing oxygen from the atmosphere and drying to an elastic skin (cross-linking) when exposed to air (oxygen) in a thin film. Melon seed oil, on the other hand, contains largely linoleic and oleic acids with an appreciable proportion of saturated acids. The oil is classified as a semidrying oil and the drying process is slower.

The chemical compositions of the oils of rubber and melon seeds show that these oils have comparable levels of unsaturation as linseed (a drying oil), and soyabean (a semidrying oil) presently used in the coatings industry. Both rubber and melon seed oils respond to the conventional refining processes of degumming, bleaching, and alkali refining. The optimum bleaching conditions of the oils using various clays, and the solvents that give high extraction yield of the oils, have been established.^{9,10}

The present study investigated the alcoholysis responses of the oils of rubber seed, melon seed, linseed, and soyabean at the reaction temperatures of 200, 220, 245, and 260°C. These temperatures cover the range generally encountered in

the commercial preparation of alkyd resins. The effects of time on the alcoholysis reaction are also reported. Linseed and soyabean oils are chosen as they are typical of drying and semidrying oils currently in use in alkyd resin synthesis.

Rubber seed and melon seed oils presently are undergoing investigations in our laboratory as possible substitutes for the imported linseed and soyabean oils currently used as the sole drying oils in the surface coatings industry in the country.

Both rubber and melon seed oils presently have no industrial importance in the country. However, there are many domestic applications of melon seeds in the country, among which are the making of the popular egusi soup and ogiri, a local spice among the Igbos. Rubber seed is yet to have any known domestic application in the country. Recently, however, an attempt by a vegetable oil processing company based in Kano, Nigeria to introduce processed rubber seed oil into the market as an edible oil was promptly stopped by the Food and Drug Administration of Nigeria because its fitness for human consumption could not be guaranteed. The rubber seeds, containing the oil, presently rot away at the various plantations each season. Newfield¹¹ in his studies had shown that the quantity of rubber seeds available in the country are more than enough to meet the rubber seed oil requirements of our oil paint industry and consequently has the potential of entering global surface coatings industrial market.

The total production of melon seeds in the country on the basis of 1992 census was put at 190,000 tonnes per year. This figure, which must have increased significantly over the years, should be able to meet a paint industry melon seed requirements for the production of melon seed oil. Melon seed has a very high oil content.

EXPERIMENTAL

The oils of melon (*Colocynthis vulgaris* Shrad) and rubber (*Hevea brasiliensis* (Kunth) Muell) seeds were obtained by solvent extraction. The oils of linseed (*Linum usitatissimum* L.) and soyabean (*Glycine max* (L) Merr) were obtained in refined states and used without further purifications. The melon seed and rubber seed oils were alkali refined using Cocks and Rede's method¹² and bleached. The iodine values of the oils were determined using ASTM method, (D 1959-69, 1982).¹³

The reaction between glycerol and the oils were carried out in a three-necked reaction kettle equipped with a variable speed stirrer, water condenser, thermometer (0-300°C), sampling device, and nitrogen inlet tube.

The kettle that had been flushed with nitrogen was charged 133.50 g of the refined oil (melon seed, rubber seed, soyabean, or linseed). The oil was heated to the reaction temperature (200, 220, 245, or 260° ± 2°C), 3.22 g of the catalyst litharge (PbO) was then added immediately followed by 30.7 g glycerol, which was added slowly from a dropping funnel over a period of 2 min with vigorous agitation. Samples were withdrawn at different reaction times and the methanol tolerance of each sample determined by noting the solubility of 1 volume of alcoholysis mixture in 2 volumes of anhydrous methanol. The alcoholysis reaction is completed when the alcoholysis mixture becomes soluble in the methanol. Each sample withdrawn is analyzed for α -monoglyceride, and free glycerol contents by the method of Pohle and Mehlenbacher.¹⁴ Polyglycerol analysis was done as reported by Tawn.¹⁵

RESULTS AND DISCUSSION

The alcoholysis responses of the oils of rubber seed, melon seed, linseed, and soyabean oils at different reaction temperatures and times are shown in Tables II and III. Tables IV and V give the polyglycerol contents of the alcoholysis mixtures of the oils at the temperatures studied.

At 200°C, the alcoholysis reactions of the oils were too slow for significant degrees of oil/glycerol interactions to occur in reasonable times. At 220°C, reactions were much faster. Temperatures of 245 and 260°C give reasonable reaction rates in the oil/glycerol reactions. It is evident from Tables II and III that the alcoholysis rate of the oils at 245 and 260°C are quite similar. For example, linseed oil had alcoholysis rate of 25 min at 245°C and 20 min at 260°C, whereas rubber seed oil had alcoholysis rate of 30 min at 245°C and 25 min at 260°C. From energy considerations alone, especially in a country like Nigeria where the cost of electricity is very high, the temperature of 245°C should represent the optimum alcoholysis temperature for the oils of linseed, rubber seed, soyabean, and melon seed oils.

Investigations on the polyglycerol contents of the alcoholysis mixture of the oils at 220, 245, and 260°C have shown the presence of small

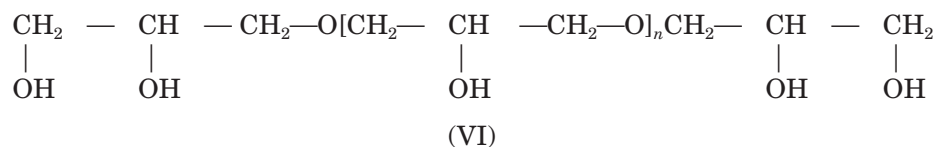
Table II Effects of Time and Temperature on the Alcoholysis of Linseed and Soyabean Oils

Temp (°C)	Time (mins)	Linseed Oil		Soyabean Oil	
		Periodate Oxidation			
		α - Monoglyceride	Glycerol	α - Monoglyceride	Glycerol
200	80	42.70	21.73	39.42	22.81
	90	43.47 ^a	18.21	41.74	21.93
	100	43.91	18.83	42.91 ^a	20.36
	110	44.25	14.51	43.36	18.69
	120	44.80	13.17	43.90	16.43
220	40	40.92	21.98	39.62	23.17
	50	42.16	20.61	40.81	21.58
	60	44.23 ^a	15.33	42.46	20.79
	70	44.38	14.80	43.41 ^a	17.91
	80	44.90	13.78	43.64	17.63
	90	—	—	44.47	15.00
245	25	43.61 ^a	19.31	41.62	21.60
	30	43.79	17.63	42.30	20.97
	40	44.20	13.69	43.00 ^a	18.23
	45	—	—	43.41	17.91
260	20	43.68 ^a	17.61	42.96	21.77
	30	44.40	13.96	43.91 ^a	15.21
	40	44.93	13.01	44.00	14.81
	45	—	—	44.60	13.87

^a First indication of methanol tolerance by alcoholysis mixture.

quantities of polyglycerols at 220 and 245°C but definite quantities at 260°C, the amount of which increased with increasing alcoholysis time (see Tables IV and V). These polyglycerols are formed from etherification reaction of glycerol, a competing side reaction during the alcoholysis process. The etherification reactions

generally are nonreversible and lead to increased functionality of the alcoholysis system and also interfere with the control and reproducibility of the alcoholysis product. Under basic catalysis (used to promote alcoholysis), polyglycerols of the type (VI) are formed.¹⁶



Commercially, it is desirable to keep the time of reaction to a minimum; on the other hand, from a technical point of view, the most reproducible process would be one in which side reactions did not occur, and the glycerol/oil reaction reaches equilibrium. The presence of small quantities of polyglycerols in the alcoholysis mixtures of the

oils at 245°C when compared with the quantity present at 260°C makes it reasonable to further consider 245°C as the optimum alcoholysis temperature for the linseed, soyabean, rubber seed, and melon seed oils. At the optimum alcoholysis temperature, there is a high degree of glycerol/oil interaction in a relatively short reaction time as

Table III Effects of Time and Temperature on the Alcoholysis of Rubber Seed and Melon Seed Oils

Temp (°C)	Time (mins)	Rubber Oil		Melon Oil	
		Periodate Oxidation			
		α -Monoglyceride	Glycerol	α -Monoglyceride	Glycerol
200	80	42.96	20.18	40.72	22.76
	90	43.71 ^a	17.33	42.37	19.91
	100	43.92	16.27	43.17 ^a	16.79
	110	44.11	14.82	43.33	15.00
	120	44.67	14.36	43.67	15.01
220	40	41.62	22.93	40.62	23.46
	50	42.96	21.37	41.90	21.09
	60	44.21 ^a	14.96	42.91	18.41
	70	44.28	14.23	43.62 ^a	16.82
	80	44.70	13.41	43.88	14.05
	90	—	—	44.01	13.33
245	25	43.82	16.0	40.27	23.61
	30	44.07 ^a	14.12	42.46	17.78
	35	—	—	42.81 ^a	17.01
	40	14.16	13.10	43.89	16.17
	45	—	—	—	—
260	20	43.09	17.17	43.0	17.76
	25	43.41 ^a	14.78	—	—
	30	44.03	14.57	43.73 ^a	14.32
	40	44.87	13.81	44.07	13.46
	45	—	—	44.71	12.76

^a First indication of methanol tolerance by alcoholysis mixture.

indicated by the α -monoglyceride content. These monoglycerides are two-dimensional polymers and in subsequent esterification reaction, lead to resins with faster drying power and improved gloss, and gloss retention.

As shown in Tables II and III, it is evident that at lower temperatures (200, 220, and 245°C) there is the preferential alcoholysis of the more unsaturated oils, rubber seed and linseed. The general alcoholysis rates observed in this study are: linseed oil \approx rubber seed oil > soyabean oil > melon seed oil.

The degree of unsaturation of the oils based on their iodine number is in the following order: linseed oil > rubber seed oil > soyabean oil > melon seed oil. The high alcoholysis rate of linseed oil has been reported. Siego et al.¹⁷ in their study on the alcoholysis of fatty oils observed the following order in alcoholysis rate: linseed oil > olive oil \cong coconut oil \cong dehydrated castor oil > soyabean oil. Ghanem et al.¹⁸ have attributed the high al-

coholysis rate of oils with high iodine numbers to a high solution capacity for glycerol in the mixed triglyceride at the reaction temperature.

The α -monoglyceride contents of the alcoholysis mixtures of rubber seed and linseed oils at methanol tolerance were in most cases similar and higher than those of soyabean and melon seed oils. This has some practical implications in the manufacture of alkyd resins. Because alcoholysis products are effective raw materials for alkyd resin manufacture it is logical to expect resins synthesized from alcoholysis mixtures of rubber seed and linseed oils (which have high α -monoglyceride contents) to produce high viscosity alkyds with better drying properties than ones prepared from alcoholysis mixtures of melon seed and soyabean oil. Melon seed oil can be brought up to the same standard by increasing alcoholysis time at 245°C to 40 min at which the α -monoglyceride content matches that of linseed oil with 25 min alcoholysis time. Based on the discussions

Table IV Effects of Time and Temperature on the Polyglycerol Contents of Linseed and Soyabean Oil Alcoholysis Mixtures

Temp (°C)	Time (min)	Linseed Oil	Soyabean Oil
		Polyglycerol Content	
220	40	0.03	—
	50	0.25	0.18
	60	0.28 ^a	0.20
	70	0.31	0.53 ^a
	80	0.46	0.65
	90	—	1.15
245	25	0.19 ^a	—
	30	0.38	0.06
	40	0.64	0.28 ^a
	45	—	0.76
260	20	0.32 ^a	0.28
	30	0.86	0.47 ^a
	40	0.56	1.21
	45	—	2.86

^a First indication of methanol tolerance by alcoholysis mixture.

above, it is therefore possible to replace linseed oil with rubber seed oil and to replace soyabean oil with melon seed oil in the synthesis of alkyd resins.

From Tables II and III it is evident that there are small variations in the α -monoglyceride contents of the alcoholysis mixtures of the melon seed, rubber seed, linseed, and soyabean oils at and after methanol tolerance. This is an indication that alcoholysis reaction is not an equilibrium reaction. The attainment of chemical equilibrium by the glycerol/oil reaction has been the subject of disagreement among some research workers. Although some workers claim that equilibrium is attained in the system,^{19,20} others claim that equilibrium is not attained in the system^{21,22} and that alcoholysis reaction is a non-equilibrium reaction.

The alcohol solubility of the alcoholysis mixtures of the oils is observed to begin at 42–45% conversion of oils to monoglyceride, corresponding to infinite tolerance for methanol.

From Tables II and III it is evident that temperature greatly affects the alcoholysis of triglycerides (oils). The higher the temperature, the faster is the alcoholysis reaction and vice versa. Increase in temperature generally speeds up

chemical reactions by lowering the activation energy, which enables reactants to form products in relatively shorter reaction times. Higher alcoholysis temperatures, however, are not recommended because at these temperatures reactions, particularly self-polymerization of the polyols, may become important.

Tables II and III show that the percent of glycerol is observed to fall steadily as more oils are converted to monoglycerides. Free glycerol in an alcoholysis mixture reacts with phthalic anhydride during alkyd resin synthesis to produce three-dimensional polymers, which can be of very high molecular weight.

CONCLUSION

The optimum alcoholysis temperature for the oils of melon seed, rubber seed, linseed, and soyabean has been determined to be 245 ± 2 °C for each of the oils. The alcohol solubility of the oils has been observed to begin at 42–45% conversion of oils to monoglycerides.

Table V Effects of Time and Temperature on the Polyglycerol Contents of Rubber Seed and Melon Seed Oil Alcoholysis Mixtures

Temp (°C)	Time (min)	Rubber Seed Oil	Melon Seed Oil
		Polyglycerol Content	
220	40	—	—
	50	0.22	—
	60	0.26 ^a	0.19
	70	—	0.30 ^a
	80	0.56	0.46
	90	—	1.26
245	25	0.16	—
	30	0.51 ^a	—
	35	—	0.38 ^a
	40	0.63	0.67
	45	—	—
260	20	0.29	0.30
	25	0.76 ^a	—
	30	1.31	0.41 ^a
	40	2.49	1.19
	45	—	2.01

^a First indication of methanol tolerance by alcoholysis mixture.

The alcoholysis reactions of rubber seed and linseed oils were found to be similar; so are those of melon and soyabean oils. This similarity therefore suggests that rubber seed and melon seed oils can replace (substitute) linseed and soyabean oils respectively in the synthesis of oil-modified alkyd resins.

REFERENCES

- Allan, G. A. *Paint Manuf* 1964, 34, 163.
- Chemistry and Processing of Alkyd Resins, Monsanto Chemicals, 27, 1962.
- Runk, R. H. *Ind Eng Chem* 1952, 44, 1125.
- Pintile, T. *Bull Teh Inform-Lab Cent Cert-Lacuri Cerneluri Bucuresti* 1970, 1, 39.
- Sathyanarayana, M. N.; Kishanprasad, V. S.; Chandrasekhar Rao, T.; Sampathkumaran, P. S.; Gedam, P. H. *Paintindia* 1994, 44(8), 31.
- Eka, O. U. *West Afr Biol Appl Chem* 1977, 20(3), 45.
- Igwe, I. O. M.Sc. Thesis, University of Nigeria, Nsukka, 1989.
- Girgis, P.; Said, F. *J Sci Fd Agric* 1968, 19, 615.
- Achife, E. C. M.Sc. Thesis, University of Nigeria, Nsukka, 1988.
- Attah, J. C.; Ibemesi, J. A. *J Am Oil Chemists' Soc* 1990, 67(1), 25.
- Newfield, B. Seminar, Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, 1982.
- Cocks, L. V.; Rede, C. V. *Laboratory Handbook for Oil and Fat Analysis*, Academic Press, London, 331, 1966.
- ASTM D 1959-69, Test for Iodine Value of Drying Oils and Fatty Acids, American Society for Testing and Materials, Philadelphia, Pa., 29, 1982.
- Pohle, W. D.; Mehlenbacher, V. C. *J Am Oil Chemists' Soc* 1950, 24, 54.
- Tawn, A. R. H. *J Oil Colour Chemists' Soc* 1956, 39(4), 235.
- Hanschid, R.; Petit, J. *Bull Soc Chim France* 1956, 878.
- Siego, I.; Morid, K.; Tadashi, W.; Hiroyuki, N. *Yukagaka* 1969, 18(11), 812.
- Ghanem, N. A.; Abd El-Mohisen, F. F. *J Oil Colour Chemists' Assoc* 1966, 49(6), 490.
- Mort, F. *J Oil Colour Chemists' Assoc* 1956, 39, 253.
- McKee, R. S.; Staddon, A. W. E. *J Oil Colour Chemists' Assoc* 1961, 44, 497.
- Shibamaya, K. *Mitsubishi Denki Laboratory Reports* 1960, 1, 97.
- Solomon, D. H.; Swift, J. D. *J Oil Colour Chem Assoc* 1966, 49, 915.
- Runk, R. H. *Ind Eng Chem* 1952, 44, 1125.