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Efficacy of Catalysts in the Batch Esterification of the Fatty Acids of *Thevetia Peruviana* Seed Oil

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ABSTRACT: The methyl, ethyl, propyl and butyl esters of the fatty acids of *Thevetia peruviana* seed oil were successfully prepared by the batch-esterification procedures. Various acid catalyst and various molar ratios of fatty acid to alcohol were investigated. H_3PO_4 was found to be ineffective to catalyze the esterification of the free fatty acid. HCl gas and conc. H_2SO_4 both proved very effective in catalyzing the reaction. Concentrated H_2SO_4 however, proved better of the two acids. Three molar ratios 1:1, 1:3 and 1:10 were investigated. 1:3 molar ratio of the free fatty acid to the alcohol was found to be the most efficient. *@JASEM*

Thevetia peruviana, more commonly known as yellow oleander or milk bush, is an evergreen, dicotyledonous shrub which is believed to have originated from the forest of tropical America, precisely from central America, but has naturalized in the tropical and subtropical regions of the world. It is abundantly available in Nigeria, where it is mainly grown as an ornamental plant. The seed of the plant contains about 60% oil, which hydrolyses to give about 64.3% oleic acid, 6.3% linoleic, 17.1% palmitic, 11.8% stearic and 0.4% arachidonic acid (Jairo, 1981). The defatted seed cake is about 30% protein but rich in toxins. The work reported in this paper aims at preparing low alkyl esters of the fatty acids of the oil for possible use as oleochemicals. Oleochemicals provide competing alternative to petrochemicals. The oils of many oil-rich-seeds e.g soybean oil, rapeseed oil and other oilseeds have been converted to simple monobasic acid esters either by the hydrolysis-esterification procedure or by direct alcoholysis (transesterification) of the oil. (Charkrabarty, 1985; Chritie, 1992; Freedman *et al.*, 1986). These low alkyl esters have found wide applications as oleochemicals - as textile fibre lubricants, rolling oils and cutting oils. They also find application as alternative fuel sources and as suppliments or even replacements to petroleum diesel. (Charkrabarty, 1985; Szpiz *et al.*, 1985; Peterson, 1994; Howard, 1994; Gateau *et al.*, 1985). The interest in oleochemicals is increasing in recent times because of the environmental friendliness, renewability and degradability of the products when compared with petrochemicals. (Staat and Rochietta, 1992; Baranescu, 1994; Morrison, 1995)

This work therefore aims at finding an economic route to the preparation of low alkyl esters of thevetia seed oil with a view to finding economic uses for the plant, which has hitherto been used merely as an ornamental plant.

MATERIALS AND METHODS

The crude thevetia seed oil (TSO) used in this study was obtained by the solvent extraction of the oil from the crushed seed using light petroleum ether (b.p 60-80^{0}C) as the solvent of extraction. The mixture was then distilled to recover the solvent and the oil was obtained as a residue of the distillation. The FFA was obtained from the oil by standard alkaline hydrolysis (AOCS, 1979). Adding dil. H_2SO_4 to form an oily fatty acid layer then acidified the resultant solution. Four different alcohols - methanol, ethanol, 2-propanol and 1-butanol were used for the esterification reaction, and three different molar ratios of fatty acid to alcohol - 1:1, 1:3 and 1:10 were investigated for each of the alcohols. Different acid catalysts - dry HCl gas, conc. H_2SO_4 and conc. H_3PO_4 were also used with each of the alcohols and at the various molar ratios. For each reaction, a 250ml two-necked round bottom flask equipped with a reflux condenser and a magnetic stir bar was charged with the molar equivalent of the FFA and alcohol. The FFA was assumed to be predominantly oleic, thus the molar mass was taken to be about 282g, and this guided the measurements. To esterify 1:1 FFA: Methanol with H_2SO_4 catalyst, 28g of FFA (about 0.1 mol) was reacted with 3.5g methanol (also about 0.1 mol) and 1.0ml conc. H_2SO_4 as catalyst. The mixture was refluxed for about 2-3 hours. The reaction was monitored at regular intervals (15min) by a titration of aliquots with 0.1M NaOH solutions. The reaction was also studied by thin layer chromatography (tlc) using 1:2 chloroform: petroleum either as developing solvent. The developed plate was visualized in an iodine chamber. This procedure was repeated with the other molar ratios, catalysts and alcohols.

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RESULTS AND DISCUSSION

The results obtained for the titration of the aliquots with 0.1M NaOH are shown in Figures 1-5 below. The slopes of the graphs are – 0.0017min^{-1}, - 0.0031 min^{-1}, - 0.0076 min^{-1}, - 0.00083 min^{-1} and - 0.0082 min^{-1} respectively. Both HCl and H_2SO_4 catalyze the esterification following the same trend but at different rates. Phosphoric acid result is not worthy of presentation because it is rather erratic. Catalysis by HCl served as control, and the results shows a steady decrease in titre values for each of the three preparations (1:1, 1:3, 1:10). The 1:10 ratio is adjudged to be the fastest. The esterification comes to equilibrium in 105 minutes. Furthermore, amount of acid that remains unreacted is lowest (16%). In all cases, there is the HCl involved in the titration, but the contribution by this is constant for every titration. There is a significant variation in the degree of conversion to the ester at zero time and when equilibrium is established. For the three preparations it is (100 - 58) = 42%, (100 - 35) = 65% and (100 - 16) = 84% respectively for the 1:1, 1:3 and 1:10 preparations.

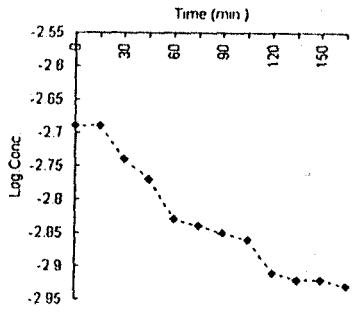

Fig.1 Esterification of 1:1 FFA/MeOH using HCl Catalyst - titration with 0.1M NaOH

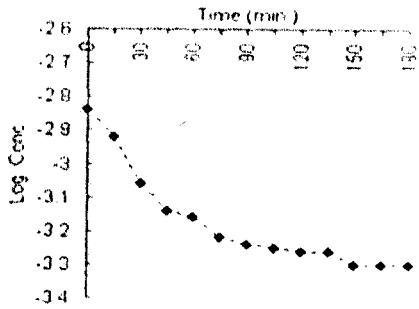

Fig. 2 1:3 FFA/MeOH, HCl catalyst - titration with 0.1M NaOH

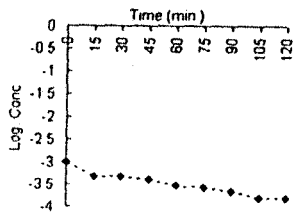

Fig. 3 1:10 FFA/MeOH, HCl catalyst - titration with 0.1M NaOH

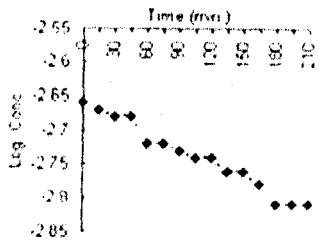

Fig. 4. 1:1 FFA/MeOH, H_2SO_4 catalyst - titration with 0.1M NaOH

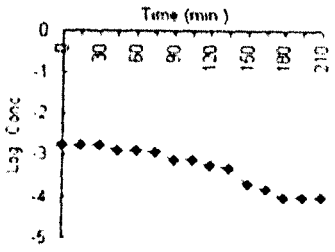

Fig. 5. 1:3 FFA/MeOH, H_2SO_4 catalyst - titration with 0.1M NaOH

For catalysis using H_2SO_4 for 1:1 preparation, the equilibrium conversion rate amounts to (100 - 70) = 30%, this performance is poorer compared with the 1:1 for HCl catalysis. The dibasicity of this catalyst (i.e. H_2SO_4) is considered to account for the overall higher titre values. The 1:3 preparation catalyzed by H_2SO_4 showed a much better result with conversion rate (100 - 5.9) = 94.1%. Batch esterification using H_2SO_4 as catalyst at ratio 1:3 and above is convincingly most efficient for the esterification of

the fatty acids of *thevetia peruviana* seed oil. The titration results for the other preparations follow the same trend. Tlc gave an equally good picture of the reaction and the conversion of the fatty acid to the ester. This procedure was adopted for the studies of the esterification with other alcohols. Tlc provides supportive evidence to the idea that H_2SO_4 is superior to HCl in the catalysis of esterification of the fatty acids of *thevetia peruviana* seed oil. Even though no quantitative analyses of the plates were done, qualitative analysis indicates that each preparation at equilibrium contains both the fatty acids and the esters. For the H_2SO_4 catalysis, the proportion in all cases for the products outweighs the unreacted fatty acids. Whereas for HCl catalyzed reactions, there is about equal proportion for the products and the unreacted fatty acids. The ratio of the product to the unreacted fatty acids in both H_2SO_4 and HCl catalyzed reactions show the same trend, which reflects a steady increase with time. The increase is however greater for the H_2SO_4 catalyzed reactions.

Conclusion: It is concluded that H_2SO_4 catalysis of esterification of the fatty acids of *thevetia peruviana* seed oil would be tried for transesterification of the oil. Transesterification is more popularly adopted for the commercial production of alkyl esters of vegetable oils

REFERENCES

Baranescu, R A (1994). Alternative fuel choices for transportation – Overview and issues. *INFORM* 5: (4) 579.

Charkrabarty, M M (1985). Interesterification Reaction of Glycerides and their industrial uses. *J. Ind Chemi. Soc.* 62: (1), 1-6.

Christie, W W (1992). Preparation of Fatty Acid Methyl Esters (FAME). *Int. News on Fats, Oils & Related* Matters (INFORM) 3: (9), 1031-1034.

Freedman, B; Butterfield, R O; Pryde, E H (1986). Transterification Kinetics of Soybean Oil. *J. Am. Oil Chem. Soc.* 63: (10) 1375-1380.

Gateau, P; Guibet J C; Hillion, G; Stern, P (1985). Use of vegetable oils and their transesterification products as diesel fuels. *Chemical Abstracts* 103: 1073552d.

Howard, L (1994). On-Road Testing of Soy Diesel. *INFORM* 5: (4) 520.

Jairo, C A (1981). Phytochemical study of the fixed oil of Theretia peruviana seeds. *Chemical Abstracts*, 95: 3414m.

Morrison, D S (1995). Biodegradable Lubricants. *Chemical Abstracts* 122: 218327w.

Official and Tentative Methods of the American Oil Chemists' Society, (1979); Vol. 1 AOCS, Champaign, IL.

Peterson, C L (1994). Rapeseed Oil Esters - Engine Testing and Demonstration *INFORM* 5: (4) 520.

Staat, F; Rochietta, C (1992). European firms increasing Biodiesel capacity. Applewhite, T.H. (Ed) *INFORM* 3: (12) 1302-1305.

Szpiz, R R; Jablonka, F H; Pereira, D A; Hartman, L (1985). Extraction of vegetable oils with ethanol followed by transesterification with this alcohol for producing fuel. *Chemical Abstract* 103: 9026r.