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NONCATALYTIC ESTERIFICATION OF INDUSTRIAL ALCOHOLIC WASTE

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A noncatalytic esterification of fusel oil was conducted. Studies including the different parameters are investigated to determine the optimum operating conditions for the production of corresponding acetates of the alcohols of fusel oil, by using the acetic anhydride instead of acetic acid to avoid the use of mineral acid as catalyst. The studied parameters were cited as: molar ratio of reactants and reaction time. The optimum conditions were found to be (2:1/ace.anh.:fusel oil) and 120 min. as molar ratio and time respectively.

Key words: Industrial alcoholic waste, Esterification, Fusel oil.

Introduction

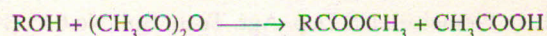
The advent of synthetic fragrances, incorporated in food industries, has led to a widespread interest in acetates of most alcohols as components in flavouring and odouring [1]. The conventional method for preparation of these esters is the reaction of the acid with an excess of alcohol in the presence of catalyst (mineral acids).

In view of manipulation of an industrial alcoholic waste, namely fusel oil, earlier studies [2,3] had reported its esterification with glacial acetic acid using sulphuric acid as a catalyst. During investigation, a need arose for yield improvement (66%), by removing the water of esterification. In addition, the use of a strong mineral acid is undesirable in the production of these acid - sensitive esters. The use of acid regenerated cation exchangers, as catalysts, for effecting esterifications had been suggested [4,5] to offer distinct advantages over conventional methods with respect to the purity of the obtained esters.

Apparently, in this particular situation, where the esters is susceptible to acid catalysis, it is preferable to conduct the reaction without catalyst. Since the most important factors influencing the direction of esterification reactions is the removal of water from reaction mixture, a number of specialized procedures have been evolved to accomplish this by adsorption, using column of desiccant mounted over the reaction vessel [6-8]. Comparisons were made with esterification using 1% sulphuric acid; in every case, the noncatalytic method gave better yields and lighter-coloured products.

However, it is well established that there is no universal manner in which all esterification reactions can be forced to completion: due consideration must be given to the particular system involved. Referring to fusel oil, as it contains alcohols mostly between C₂-C₅ as the major constituents, the use of desiccants will be probably unsuccessful due to the adsorb-

ent selectivity for individual alcohols. Attention has been made to esters from acid synthesizing acetate esters from fuel oil, using acetic anhydride have been explored with the object of finding a simple and efficient method for making these esters according to the following equation:



The acetic acid produced can not hydrolyse the ester, and hence the reaction may goes to completion.

The ultimate goal of the present work is to give an integrated picture of the parameters influencing the esterification reaction, namely molar ratio and reaction, time.

Experimental

Initially, the crude fusel oil, provided by the Egyptian Sugar and Distillation Company, was dehydrated over calcium oxide, and its chemical composition was determined by gas chromatography [2] which is as follows:

Ethyl alcohol	3.96% mole
Iso-butyl alcohol	5.28% mole
n-Butyl alcohol	9.61% mole
Amyl alcohol	76.86% mole

The reaction is essentially influenced by the following two main factors: (a) Molar ratio of acetic anhydride to fusel oil and (b) Reaction time.

The reaction temperature is considered constant at the mixture boiling point ($\approx 110^\circ\text{C}$). The experimental set-up consists simply of a 500 ml pyrex flask equipped with a reflux condenser, mercury thermometer and a magnetic stirrer to ensure perfect mixing. A well-thermally controlled hot plate was used to supply the necessary heat flux. After preheating, the determined amounts of acetic anhydride and fusel oil were mixed and rapidly heated to refluxing (less than 10 min.),

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thereafter, the thermostat was regulated to maintain constant temperature. At the end of the run, the reaction was stopped by sudden quenching in an ice bath. An equal volume of water was added to the reaction mixture for extracting the unreacted anhydride as well as the acetic acid formed. The resulted two phases were then submitted to a gas chromatographic analysis for individual identification of the reaction products, both quantitatively and qualitatively.

Results and Discussions

For the quantitative analysis of the reaction mixture, the retention time of each compound was determined with the use of authentic samples while the quantitative analysis was carried out using the peak area technique which was calculated by the computer system attached to the gas-liquid chromatography apparatus. All the results proved their consistency and reliability by material balance within $\pm 3\%$ accuracy.

Dependence of the reaction products on the molar reactants ratio. To investigate the effect of molar reactants ratio on the esterification reaction, a molar ratio of acetic anhydride to fusel oil, ranging from 0.5/1 to 5/1 was employed at a constant reaction time of 120 min. The results obtained are illustrated in Fig. 1 through Fig. 3. From Fig. 1 and 2, it can be seen that the lower reactants ratio corresponds to a minimum residual in ethyl and butyl alcohols giving the highest yield, and the higher reactants ratio corresponds to a maximum conversion in amyl alcohol. This is attributed mainly to different sequence of reactions occurring and different initial concentration of alcohols in fusel oil, together with the dependence of the esterification limits upon the structure of the molecules involved. Considering the global trend of esters formation with molar reactants proportions

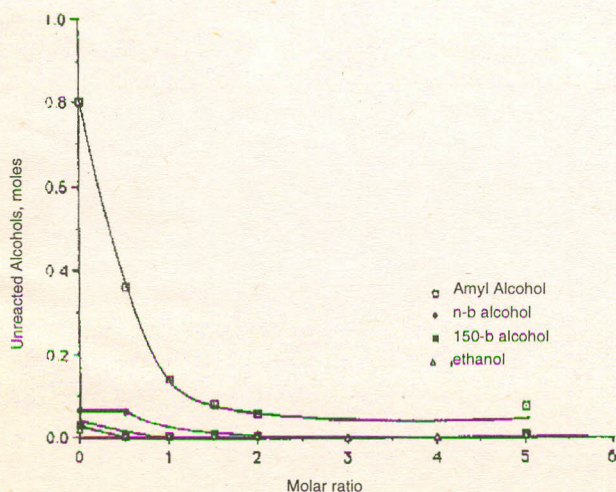


Fig. 1. Unreacted alcohol vs. molar ratio.

in (Fig. 3), it could be concluded that the optimum range for acetates is obtained at 2 acetic anhydride : 1 fusel oil molar ratio.

Dependence of the reaction time on the esterification products. The rates of formation of individual acetates from fusel oil are illustrated in Fig. 4. within the interval time of 5 min. to 120 min., the evolution of these products is characterised by a rapid increase in butyl acetates and a moderate increase in ethyl and amyl acetates, reaching highest yield (9-97%) after 120 min, while the former esters reach 80-95% yield after 10-15 min. Table 1 demonstrates a comparison between the yield of individual esters obtained from the present work, with that from the previous study [2] considering acid catalysis.

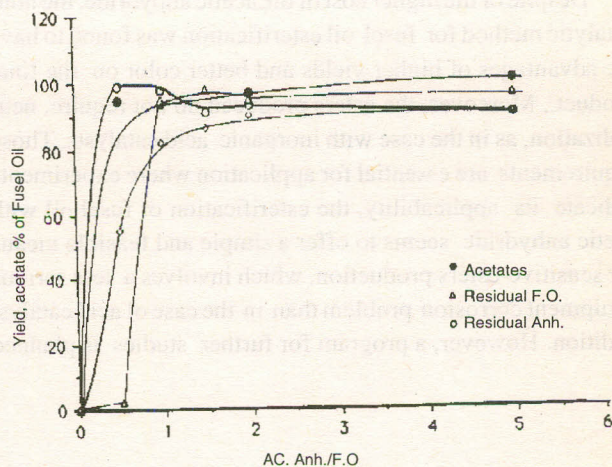


Fig. 2. Distribution of individual esters function with molar reactants ratio.

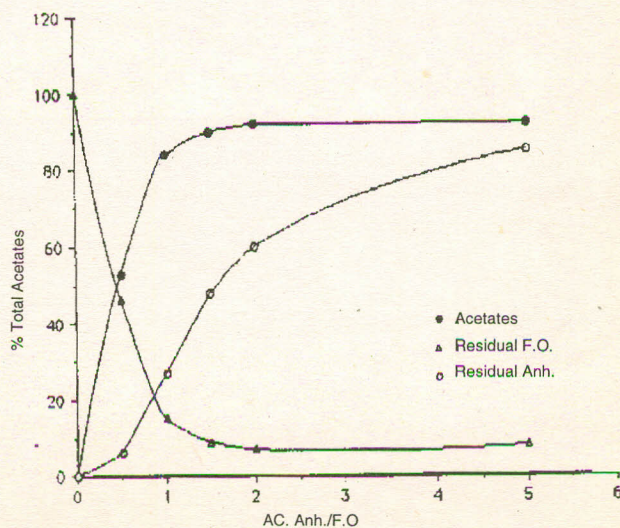


Fig. 3. Relation between the reaction mixture ratio.

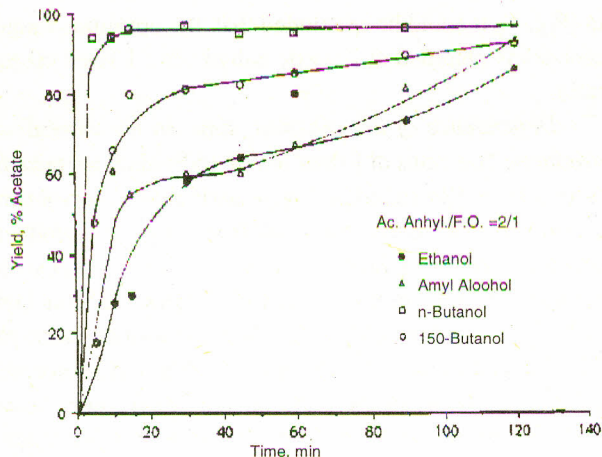


Fig. 4. Acetates yield vs. time.

Conclusion

Despite of the higher cost of the acetic anhydride, the non-catalytic method for fusel oil esterification was found to have the advantages of higher yields and better color on the final product. Moreover, the esters produced do not require neutralization, as in the case with inorganic acid catalysts. Those requirements are essential for application where experiments indicate its applicability, the esterification of fusel oil with acetic anhydride seems to offer a simple and feasible means for sensitive-esters production, which involves a less serious equipment corrosion problem than in the case of acid catalyst addition. However, a program for further studies is planned

TABLE 1. YIELDS PERCENT OF CATALYTIC AND NONCATALYTIC ESTERIFICATION.

Esters	Ethyl acetate		n-Butyl acetate		Iso-Butyl acetate		Amyl acetate	
	Cat.	Non-Cat.	Cat.	Non-Cat.	Cat.	Non-Cat.	Cat.	Non-Cat.
% yields (based on acetates produced)	11.8	1.5	13.4	2.5	3.8	7	71	89

in order to establish the proper large-scale production method, technically and economically.

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