Improved Method for Rosin and Fatty Acids in Tall Oil

E.E. BALDER and **E.P. CROWELL**, Union Camp Corporation, Research and
Development Division, Princeton, New Jersey 08540

ABSTRACT

An analytical procedure is presented for determination of the rosin and fatty acid contents of tall oil products. Rosin acids are determined by titration after selective esterification of the fatty acids at room temperature with anhydrous methanolic hydrochloric acid reagent. The fatty acid content is calculated by difference from acid number and rosin acid determinations. The method presented has smaller sample requirements, shorter analysis time, greater selectivity, and improved precision above 15% rosin acid compared to standard procedures. The standard deviations for the determination of percent rosin and fatty acids have been found to be 0.30 and 0.34, respectively, over the entire concentration range. The reaction mechanism of acid catalyzed esterification is discussed with respect to the reaction rates and selectivity. The esterification variables which were investigated include catalyst concentration, sample size, reaction time, selectivity, and effect of water.

INTRODUCTION

The literature reports several methods for the analysis of mixtures of fatty and rosin acids. These methods rely on the quantitative conversion of the fatty (primary) acids to a nontitratable species leaving the rosin (tertiary) acids available for volumetric measurement. The fatty acid content then is calculated by difference from the total acid content.

The most widely used methods are the modified Wolff method, American Society for Testing and Materials (ASTM) D1585-63 (1), for samples with greater than 15% rosin and the Herrlinger-Compeau method, ASTM D1240-54 (1), for low levels of rosin acid. Both methods employ methanol with sulfuric acid as the catalyst and reflux reaction conditions. The modified Wolff method was investigated by Sheers and Stevenson (2). They present data which show a 2.4% reaction of rosin acids under the specified conditions, which is undesirable. To account for the accuracy of their data, it must be assumed that the esterification of fatty acids is incomplete by a similar amount. This conclusion resulted in our concern as to the applicability of this method for tall oil process samples.

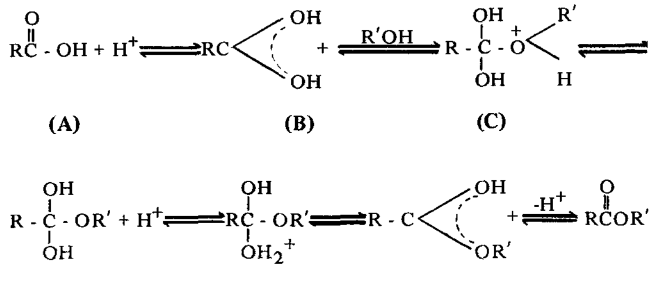
The Herrlinger-Compeau method for low levels of rosin acids has been shown to have excellent precision (3) but requires a large sample and a time consuming liquid-liquid extraction of the mineral acid catalyst. The micromethod of Crowell and Burnett (4) has been found to be applicable to samples containing a wide range of component concentrations. Their method requires a minimum of sample but requires extraction of the excess reagent. A variety of other methods reported in the literature has been used for this analysis, but none appears to offer the speed, selectivity, and precision desired for our laboratory studies.

All of the reported procedures are based upon the acid-catalyzed esterification of fatty acids, but reaction conditions vary considerably among methods. Our approach has been to consider the reaction mechanism of the esterification and to explore experimentally the reaction conditions in terms of completeness of fatty acid esterification and minimization of rosin acid reaction. An additional consideration is the analytical time required for determination. The most time consuming step in many of the methods is the extraction of mineral acid catalyst. Several of the methods employ a direct neutralization of the catalyst as part of the titration of the rosin acid. In this titration, two potentiometric inflections are observed, and the difference between the two is a measure of the rosin acid. The inherent difficulty with this procedure is obtaining an accurate measure of low levels of rosin acid. It would appear that the use of a strong acid catalyst, proper solvent selection, and a dilute titrant would permit measurement of low rosin acid concentrations if a selective esterification procedure could be established.

Mechanism of Acid Catalyzed Esterification

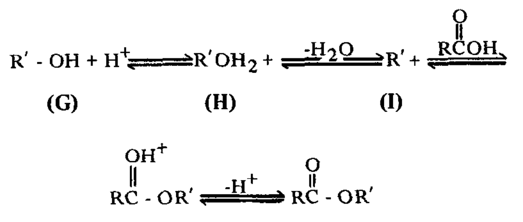
The various methods for the determination of rosin acids are based upon the selective acid catalyzed esterification of the primary acids.

A variety of possible mechanisms for this general reaction is discussed by Euranto (5). The most generally accepted mechanism is considered to be the bimolecular acyl oxygen fission as given in equation I. The rate limiting step in this mechanism is the attack of the alcohol on the protonated carboxylic acid (B). The selectivity of the reaction also arises from this attack. Since the protonated rosin acid species is more sterically hindered to the attack by the alcohol, this reaction proceeds at a much slower rate for rosin acid than for fatty acids. The reaction continues with a proton transfer and loss of water. Since the reaction is reversible, the equilibrium concentrations of the acid and ester are affected by the presence of water, but it generally is felt that a large excess of alcohol which can be employed in the analytical application of this reaction is sufficient to drive the reaction to completion (5). Literature data in support of this mechanism show that reaction selectivity is observed for closely related compounds of intermediate steric hinderance (6), increasing temperature increases the reaction rate but adversely affects the selectivity (7,8), and the reaction rate is ca. proportional to acid concentration and is reduced as the size of the alcohol is increased (5).



(I)

A second possible mechanism is the unimolecular alkyl oxygen fission as given in equation II.



(II)

TABLE I

Calculated Average Mol Wt for Tall Oil Process Samples

Sample type	Percent fatty acid	Percent normalized palmitic acid	Average mol wt calculated	Percent bias in assuming mol wt = 282.5
Crude tall oil	45	7	279	1.3
Main stream first tower	49	2	280	0.9
Crude fatty acid	92	1	281	0.6
Purified fatty acid	98	0	281	0.5
First odor cut	79	54	267	5.6
Second odor cut	75	22	275	2.9
First condenser skimmings	42	50	268	5.0
Second condenser skimmings	23	31	275	2.7

Here, the rate limiting step in the reaction is the loss of water from the protonated alcohol (H) to form the carbonium ion (I). This formation is very slow for primary alcohols. The carbonium ion then can react with the carboxylic acid to form the protonated ester (J). This reaction is rapid and probably is not as sterically hindered as the attack in the bimolecular mechanism. Therefore, reaction conditions favoring this mechanism would lead to a loss of selectivity in the esterification. The carbonium ions in solution also are free to attack the alcohol or the anion to form by-products. Support for this competing mechanism comes from our observation of the formation of methyl chloride and loss of acid strength in methanolic HCl solutions. Hardy, et al. (9) found that appreciable amounts of butyl chloride and di-1-butyl ether were formed during the esterification of amino acids with butyl alcohol-HCl reagent. These data confirm that this second mechanism is involved in the esterification and is favored by elevated temperatures.

Methanolic Hydrochloric Acid Esterification

The original method for the determination of rosin acids in tall oil as reported by Twitchell (10) employed a room temperature esterification catalyzed by HCl gas bubbled into the ethanolic solutions. Smith (7) and Sniegoski (6) studied the esterification of fatty acids using methanolic HCl reagent. From their data, it is apparent that there is a favorable reaction rate for primary acids at room temperature. This would permit elimination of reflux reaction conditions, simplifying the determination, and the lower reaction temperature should improve the selectivity of the reaction. These considerations led us to conclude that a method similar to the modified Wolff procedure could be based upon methanolic HCl esterification.

EXPERIMENTAL PROCEDURES

Materials and Equipment

Tall oil rosin acid was purified from commercial rosin acid by successive recrystallization from acetone. Tall oil fatty acids were purified by fractional distillation. Each was purified until they were 98^+% pure by gas chromatographic and wet chemical analyses. Dehydroabietic acid with a purity of 99^+% was prepared by the method of Halbrook and Lawrence (11). All other chemicals were reagent grade and used without further purification.

0.5 and 0.05N Ethanolic KOH titrants were prepared using Formula 3A alcohol and were standardized potentiometrically with benzoic acid. 6-8N Anhydrous methanolic HCl was prepared by bubbling dry HCl gas into anhydrous methanol and cooled with an ice bath. The reagent was stored at 0 C in a loosely stoppered reagent bottle inside a closed polyethylene container containing sodium carbonate absorbant. The reagent was stable for ca. 2 months.

Potentiometric titrations were performed using a recording automatic titrator equipped with an all Teflon and glass delivery system, a 10 ml burette, and miniature glass and reference electrodes.

Rosin Acid Procedure

For samples containing less than 60% rosin acids, 2 g portions were weighed into 125 ml Erlenmeyer flasks. Portions (1 g) were taken for samples with higher rosin acid concentrations. The samples then were dissolved in 50 ml anhydrous methanol. For some samples, addition of 25 ml benzene was required to achieve solution. Methanolic HCl reagent (2 ml) was added, and the flask was stoppered. After allowing the mixture to react for 30 min at room temperature, the excess HCl in the sample was neutralized with 1.5 N methanolic KOH to ca. pH 2.5. This is just prior to the mineral acid break. The mixture was titrated using standardized 0.5 N ethanolic KOH. For samples containing less than 10% rosin acid, 0.05 N ethanolic KOH titrant was used. The titrant volumes were measured between the two inflections which occur at apparent pHs of ca. 4.5 and 10.0. The rosin acid content was calculated by equation III.

$$\% \text{ Rosin Acid} = \frac{(V\text{-}V_B) \times N \times 30.2}{W}, \qquad \text{(III)}$$

where: V and V_B = the titration volumes for the sample and solvent blank, respectively; N = titrant normality; W = sample wt (g); and 30.2 = acid value for abietic acid in g/meq x 100.

A 1.5 g sample of palmitic acid was run daily using the above procedure to ensure the esterification of fatty acids was complete. The reaction efficiency was calculated using equation IV.

$$\% \text{ Esterification} = 100\% - \frac{(V\text{-}V_B) \times N \times 100\%}{W \times C}, \qquad \text{(IV)}$$

where: C is the acid value in meq/g of the sample (3.90 for palmitic acid). If the percent esterification was found to be less than 99.6%, this was taken as an indication that the reagent was too old or the methanol was not sufficiently dry.

Determination of Fatty Acid

The acid number of the sample was determined by potentiometric titration. The fatty acid value then is calculated using equation V.

$$\text{Fatty Acid Value (meq/g)} = \frac{\text{Acid Number}}{56.1} - \frac{\% \text{ Rosin Acid}}{30.2} \qquad \text{(V)}$$

The fatty acid value can be calculated as percent fatty acid if the average mol wt is known. For mixtures, this can be established by gas chromatographic analysis of the individual fatty acid distribution.

The calculation of the average mol wt for several tall oil process samples is given in Table I. For typical crude tall oil, main distillation stream, and fatty acid samples, the average mol wt is nearly equal to that of oleic acid, the major fatty acid component. Therefore, the results for these types of samples can be calculated by equation VI

TABLE II

Effect of Water Addition upon Esterification

Water added (mmoles)	Total water after reaction (mmoles)	Percent esterification
0.0	6.3	99.8
2.3	8.6	99.6
5.5	11.8	99.9
11.1	17.4	99.1
22.2	28.5	97.9
44.4	50.7	94.0
88.8	95.1	77.3

TABLE III

Analysis of Mixtures of Known Concentration

Rosin acid			Fatty acid		
Actual	Determined	Δ	Actual	Determined	Δ
98.0	97.8	-0.2	0.0	0.1	+0.1
90.0	90.3	+0.3	9.8	9.6	-0.2
46.0	46.3	+0.3	52.9	52.5	-0.4
33.3	33.3	0.0	65.3	65.0	-0.3
16.0	15.8	-0.2	82.3	82.5	+0.2
0.0	0.2	+0.2	98.0	97.8	-0.2

TABLE IV

Short and Long Term Precision of Methods

Statistical parameter	Percent rosin acid	Acid number	Percent fatty acids
Short term			
Standard deviation	0.30	0.33	0.34[a]
Number of samples	91	56	
Number of replicates	3	2	
Long term			
Standard deviation	0.32	0.26	0.36[a]
Number of determinations	17	19	

[a] Calculated by addition of variance.

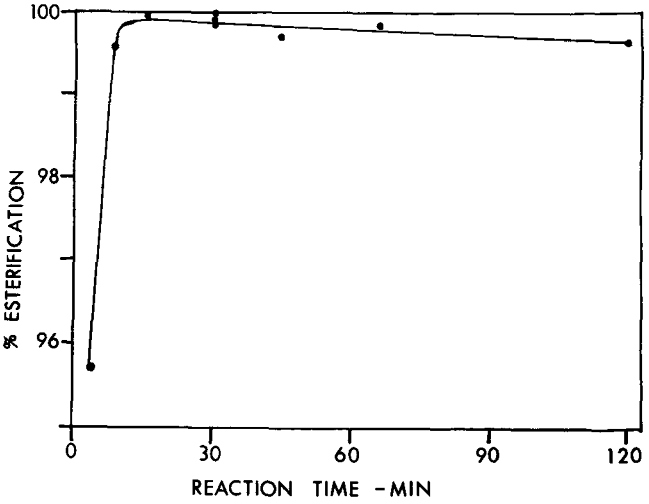


FIG. 1. Effect of reaction time upon esterification of palmitic acid.

which assumes a mol wt of 282.5.

$$\% \text{ Fatty Acid (oleic)} = 0.503 \text{ (Acid Number} - 1.86 \times \% \text{ Rosin Acid)} \qquad \text{(VI)}$$

For samples which contain a large amount of lower mol wt acids, i.e. palmitic acid, the error in the assumption of mol wt has a significant effect upon the calculated mol wt, and therefore, equation VII must be used.

$$\% \text{ Fatty Acids} = \text{Fatty Acid Value} \times \frac{\overline{\text{MW}} \times 100\%}{1000} \qquad \text{(VII)}$$

RESULTS AND DISCUSSION

To evaluate the effects of the various parameters upon the analytical method, each of the variables has been evaluated selectively. The factors favoring complete esterification of fatty acid were investigated using a 1.5 g sample of palmitic acid and the standard conditions of the above rosin acid procedure, except as noted.

The effect of reaction time upon the methylation of palmitic acid is shown in Figure 1. The data show that conversion to the ester essentially is complete (99.9%) in 15 min and better than 99.6% between 7 min and 2 hr demonstrating that reaction time is not critical.

The effect of HCl concentration upon fatty acid esterification is shown in Figure 2. These data indicate that the esterification is complete in 30 min at an acid concentration of ca. 1.2 moles catalyst/mole fatty acid and above. Below 1.2 moles/mole, the percent esterification after the 30 min reaction drops substantially, indicating that the effective catalyst concentration must drop off rapidly below this level. The effect is attributed to the water present in the reaction mixture which reduced the protonated carboxylic acid concentration in solution by formation of hydronium ions.

The effect of water upon the esterification was investigated, and the results are shown in Table II. Under the standard reaction conditions, ca. 6.3 moles water are contributed by the solvent, reagent, and reaction product water. The data show that an additional 5.5 mmoles (0.1 ml) water has no effect upon the degree of esterification in 30 min. Above 11.8 mmoles total water in the system, the degree of esterification drops off under these reaction conditions. These data support the hypothesis that the water effectively lowers the hydrogen ion catalyst concentration and, therefore, has a significant effect when it is in excess of the acid catalyst concentration. Considering these results, it is very important to recognize the contribution of water from the solvent, since a water content of greater than 0.2% could inhibit the reaction under the given conditions.

The effect of sample size upon the methylation of fatty acids also has been investigated. These data verified that the reaction conditions employed are sufficient for complete (99.8%) esterification of up to 3 g fatty acid and that the degree of esterification is constant over the entire concentration range.

Since a satisfactory analytical method requires esterification conditions which provide essentially complete reaction of the fatty acid and essentially no reaction of the rosin acid, the effect of the esterification conditions upon rosin acids was investigated. In this study, 0.1 g samples of purified dehydroabietic acid were reacted under the same conditions employed for the study of the methylation of palmitic acid. The percent esterification was calculated using equation IV, where C is 3.30 meq/g for dehydroabietic acid. Figure 3 presents a comparison of the esterification of rosin acids using the proposed reaction conditions and those of the modified Wolff method with various reaction times. The sulfuric acid catalyzed reaction data are those of Sheers and Stevenson (2). Room temperature esterification with methanolic HCl gave no observable esterification of rosin acid after 30 min. Only 0.2% conversion was evident after 4 hr. In contrast, esterification with refluxing sulfuric acid in methanol shows that 2.4% of the rosin acid reacted in 30 min. Our data confirm the previously stated effect of reaction temperature and demonstrate the superior selectiv-

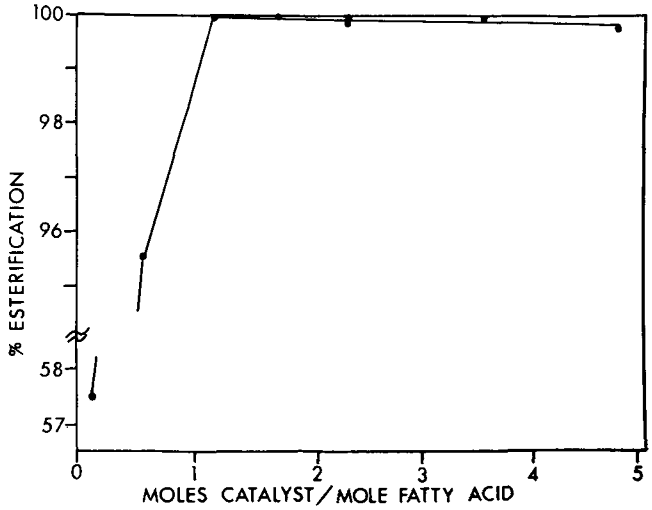


FIG. 2. Effect of catalyst concentration upon the esterification of palmitic acid.

ity of the methanolic-HCl method.

Precision and Accuracy

The accuracy of this method for analysis of the acid components of tall oil was established by analysis in triplicate of mixtures of known composition prepared by blending purified tall oil fatty and rosin acids. The results of the study are given in Table III. These data shown that there is no significant bias in the rosin and fatty acid determinations in the entire concentration range.

The precision of the proposed method as presented in Table IV was established by replicate analysis of a variety of tall oil samples. These data show the average standard deviation for the rosin acid and acid number determinations are 0.3 and 0.33, respectively. The fatty acid determination is shown to have a standard deviation of 0.34 which was calculated by addition of the variance contributed by the rosin acid and acid number determinations. The long term precision was determined by repeated analysis of a sample over a 2 month period. These data show there is no significant difference between the short and long term precisions in the proposed procedure.

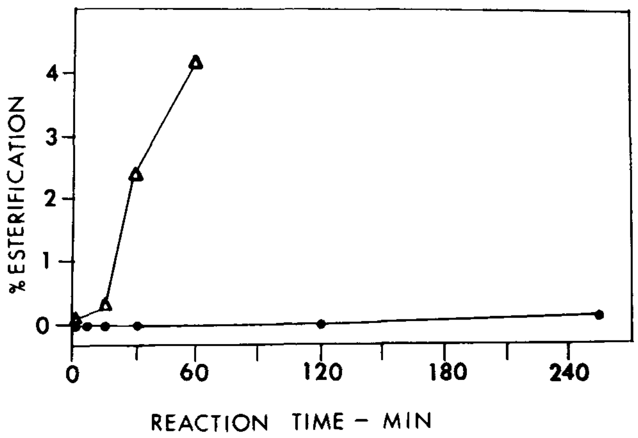


FIG. 3. Methylation of rosin acid at various reaction times. ● = Room temperature reaction, HCl catalyst and △ = reflux reaction, H_2SO_4 catalyst.

ACKNOWLEDGMENTS

N.E. Lawson prepared the dehydroabietic acid, and C.H. Mao purified the tall oil fatty and rosin acids.

REFERENCES

1. American Society for Testing and Materials, ASTM Standards, American Society for Testing and Materials, Philadelphia, Pa., 1964.
2. Sheers, E.H., and L.S. Stevenson, Tappi 43:190 (1960).
3. Herrlinger, R., JAOCS 36:119 (1959).
4. Crowell, E.P., and B.B. Burnett, Tappi 49:327 (1966).
5. Euranto, E.K., in "The Chemistry of Carboxylic Acids and Esters," Edited by S. Patai, Interscience Publishers, New York, N.Y., 1969.
6. Sniegoski, P.J., J. Chrom. Sci. 10:644 (1972).
7. Smith, H.A., J. Amer. Chem. Soc. 61:254 (1939).
8. Smith, H.A., Ibid. 62:1136 (1940).
9. Hardy, J.P., S.L. Kersin, and S.L. Manatt, J. Org. Chem. 38:4196 (1973).
10. Twitchell, E.J., Soc. Chem. Ind. 10:804 (1891).
11. Halbrook, N.J., and R.V. Lawrence, J. Org. Chem. 31:4246 (1966).

[Received June 5, 1974]