Study in fatty acids of tall oils and their products of esterification by the method of IR spectrometry for analytical control of preparation of esters

A S Govorin, N P Konovalov and N D Gubanov
Irkutsk National Research Technical University, Russia
Corresponding author’s e-mail: govorin.aleksandr@yandex.ru

Abstract. Tall oil fatty acids are a by-product of the sulfate pulping of cellulose. The field of application of tall oil fatty acids is currently limited to the production of polyhydric alcohol esters (glycerol, etriol, and pentaerythritol, primarily, for the production of alkyds); ethanolamides; disproportionated and dimer acids (including amides based on them); imidazolines; salts; as well as lower alkyl esters. However, tall oil fatty acids have the potential to be used as a basis for the synthesis of motor oils and their additives, additives to diesel fuel, as well as raw materials for the production of biodiesel fuel.

1. Introduction
Tall oil fatty acids (TOFAs) are a mixture of various substances, which in addition to carboxylic aliphatic saturated and unsaturated acids contain insignificant amounts of resin and unsaponifiable compounds. In the production of diesel fuels that comply with the world ecological standards, TOFAs have found application as an antiwear additive to fuels after the hydrofining process that they need [1], [2], [3]. There are methods for isolation of individual substances from TOFAs; however, they are multistage and require high energy consumption, which in turn seriously affects the economy of the process, and taking into account an increased interest in developments having high rates of energy and resource saving, the technologies proposed earlier can be considered as obsolete and not meeting modern world challenges [4]. The objective of this study is to develop technology that uses TOFAs or other types of fatty acids as raw materials, which will make it possible to introduce high-quality and environmentally friendly products in the fuel and energy market, as well as more efficiently use natural resources of the Russian Federation.

2. Materials and Methods

2.1 Raw materials, reagents, catalyst
For the study, TOFAs of the Bratsk Pulp and Board Mill for coniferous and mixed (coniferous and hardwood) species of trees were used. Normal alcohols, i.e., n-butanol and 1-hexanol, were used as reagents. Amberlyst-15wet-L ion exchange resins (H+ form) [5] were used as a catalyst for the process of obtaining esterification products.
2.2 Method
The raw materials and products of esterification were analyzed by the method of IR spectrometry. The spectra were recorded relative to air on an ATR FTIR mounting attachment of an IRAffinity-1S spectrometer.

3. Experimental Section
The IR spectral analysis of TOFAs of the Bratsk Pulp and Board Mill for mixed (hardwood and coniferous) species of trees (Figure 1.a) and TOFAs for coniferous trees only (Figure 1.b) was carried out, as well as the products of TOFA esterification with n-butanol (Figure 1.c), 1-pentanol, and 1-hexanol (Figure 6) were analyzed.

4. Results and Discussion
In view of the substantially complete identity of IR spectra of TOFAs for mixed type trees (Figure 1.a) and trees of coniferous species (Figure 1.b), let us consider in more detail only one of them, i.e., the IR spectrum of TOFAs for the trees of mixed type in Figure 2.
Figure 2 shows a strong band within the range of 1760–1680 cm⁻¹ having a high intensity (with a peak value of 1700 cm⁻¹) corresponding to the stretching vibrations (st.) of the C=O group. The specified range indicates a possible presence of the following groups in TOFAs: saturated aliphatic acids (–CH₂-COOH), having corresponding ranges ~1760 cm⁻¹ (monomers), 1725–1700 cm⁻¹ (dimers); α,β-unsaturated acids (C=C-COOH), having corresponding ranges ~1720 cm⁻¹ (monomers), 1715–1680 cm⁻¹ (dimers); and aromatic acids (Ar-COOH) ~1720 cm⁻¹, 1700–1680 cm⁻¹ (dimers). The existence of these groups is confirmed by the presence of the intensity of 1700 cm⁻¹.

Carboxylic acids contained in TOFAs are present in the form of associates due to hydrogen bonds [6],[7] which are confirmed by the presence of absorption bands within the range of 1420 cm⁻¹ and 1300–1200 cm⁻¹ caused by the interaction between planar deformation vibrations (ip.δ.) of O-H groups and stretching vibrations (st.) of C-O groups of dimers, as well as a wide absorption band of 940 cm⁻¹ caused by nonplanar deformation vibrations (oop.δ.) of the O-H group of the dimer.

Also, a characteristic for determining dimers of carboxylic acids is the presence of a group of absorption bands within the range of 3000–2500 cm⁻¹. In Figure 2, the highest-frequency absorption band 2920 cm⁻¹ is caused by stretching vibration (ν) of OH groups, and the band of 2850 cm⁻¹ is a combined frequency of the principal vibration in the region of 1420 cm⁻¹.

It is known that TOFAs usually include: oleic, linoleic, α-linolenic unsaturated, and stearic saturated carboxylic acids, as well as some resin acids and unsaponifiable substances [8].

![Structure formulas of carboxylic acids of TOFA mixtures](image)

Figure 3. Structure formulas of carboxylic acids of TOFA mixtures

The main structural difference between carboxylic acids being in the composition of TOFAs consists in a number of double bonds. Accordingly, oleic acid has one double bond at the 9th carbon atom (Figure 3.a), linoleic acid (Figure 3.b) has two double bonds at the 9th and 12th carbon atoms, α-linolenic acid (Figure 3.c) has three double bonds at the 9th, 12th, and 15th carbon atoms, while stearic acid has no double bonds in its molecular structure (Figure 3.d).

In Figure 2, the absorption band of 720 cm⁻¹ caused by rocking vibration of the methylene chain characterizes the n-alkyl chain in the spectrum, which indicates the presence of saturated carbon atoms from C₁₇ to C₃₆ in the mixture of TOFAs. It is impossible to determine the exact number of carbon atoms using the IR spectrum shown in Figure 2. This is due to the fact that the spectrum of TOFAs does not contain characteristic groups of weak bands, the number of which could help to determine the length of the carbon chain, in view of its state of aggregation. Methylene chains have a stable trans-conformation in the crystalline state, while in the liquid state they have a large number of
non-characteristic conformations [9]. However, according to literature data, it is arguable that the stearic acid (Figure 3.d) is present in the TOFA composition.

In addition to this, the frequency shift (ν) in the CH₂ group within the range of 3020 cm⁻¹ indicates the presence of an unsaturated =CH- group.

The planar deformation vibration of the -OH group within the range of 1420 cm⁻¹ is caused by stretching vibrations of the C-O group, while the vibration of the methylene group adjacent to the carboxyl should appear as a weak baseline in the region of 1430 cm⁻¹. However, Figure 4 shows the absence of a baseline left to the 1420 cm⁻¹ band (the contour of the missing baseline is shown in Figure 4 by a red dashed line).

![Figure 4](image)

**Figure 4.** Range of 1510–1100 cm⁻¹ in the IR spectrum of TOFAs

A very weak absorption band within the range of 1445–1430 cm⁻¹ indicates the presence of the -CH₂- group that is located between two multiple bonds, i.e., the -CH₂-C=C group. Thus, it may be concluded that in the mixture of TOFAs, in addition to the stearic acid, there is an unsaturated carboxylic acid having two multiple bonds, i.e., linolenic acid (Figure 3.b).

Also, in Figure 4, absorption bands are observed within the range of 1470, 1380 cm⁻¹, which indicates the presence of methyl groups that are a constituent part of the structure of carboxylic acids (Figure 3).
Figure 5. IR spectrum of the product of esterification with n-butanol

Figure 5 shows the IR spectrum of the product of esterification with n-butanol. A range from 1800 to 1000 cm⁻¹ underwent a significant change in the spectra after carrying out esterification, which is clearly shown in Figure 1.

The presence of esters in the esterification product is indicated by the peak at 1738 cm⁻¹ caused by the stretching vibration of the C=O group of esters. Two bands within the range of 1300–1050 cm⁻¹ are the result of asymmetric and symmetric stretching vibrations of the ester group (C-O-C), respectively.

Similar vibrations of peaks are observed in the samples obtained by the esterification of TOFAs with 1-hexanol at the same conditions at which the product of esterification with n-butanol was obtained. The IR spectrum of the product of esterification with 1-hexanol is shown in Figure 6.

Figure 6. IR spectrum of the product of esterification with 1-hexanol
5. Summary and Conclusion

Thus, IR spectrometry is one of the key analytical methods in the synthesis of ester compositions based on fatty acids, irrespective of the type of the selected reagent. The key indicator in the detection of esters in the analyzed mixture is the presence of the peak of 1738 cm⁻¹, as well as bands within the range of 1300–1050 cm⁻¹, the presence or absence of which can help to estimate the success in carrying out the process.

The obtained esterification products can be used as an antiwear additive to diesel fuel having a low sulfur content. Also, the separation of certain fractions of esters from esterification products and adding them to the diesel fuel results in a decrease in the chilling temperature of diesel fuel [10].

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