Esterification of tall oil fatty acids using ion exchange resins in order to produce energy-efficient engine oil

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Abstract. The article describes results of studies on the use of tall oil fatty acids (TOFA) when developing a method for producing esters to synthesize highly productive engine oil and additives. The article deals with the use of TOFA derivatives in the engine oil production industry. The process is efficient and safe for humans and the environment. Experiments on liquid TOFA esterification were conducted. As a catalyst, three types of ion exchange resins were used: Lewatit, Amberlite, and Tokem-100. Raw materials and reaction products were analyzed according to the federal standards for engine oils. Qualitative comparisons with Motul engine oil were carried out. The main research problems, tasks and methods were formulated.

1. Introduction and Background

Researchers from various industries study fatty acids. For example, there are works on epoxy fatty acids [1]. Some researchers believe that plant oils can be an equivalent, renewable and environmentally friendly alternative to oil materials [2]. In the Russian Federation, the most common industrial method for cellulose production is the sulfate method which is the most effective and economical [3]. One of the by-products of cellulose sulfate cooking is TOFA which is a mixture of oleic, linoleic and linolenic carboxylic acids [4]. They can serve as an alternative to plant sources of carboxylic acids.

TOFA derivatives have a wide range of applications. For example, there are studies on the use of TOFA esters as biodiesel [5]. TOFA esters can be used as lubricants or additives. In case of boundary lubrication in internal combustion engines, the friction force and wear depend on the resistance of the adsorbed film and the interaction force of the engine oil molecules with the metal surface, i.e., on oil lubricity and stickiness [6]. TOFA esters have polar molecules [7], which "stick" to metal surfaces of engine parts (the friction zone) forming an adsorbed oil film. Formation of a strong oil film makes it possible to use less viscous engine oil. Less viscous oil based on butyl esters will contribute to the same lubricating effect as oil with higher viscosity.

2. Materials and Methods

2.1 Raw materials

TOFA produced by Bratsk pulp and paper mill were used as raw materials. Two types of raw materials were analyzed: mixed (a mixture of deciduous and coniferous trees) and fatty acids of coniferous trees. The study was carried out in accordance with the federal standards. The results are presented in Tables 1 and 2.
Table 1. Quality of mixed TOFA.

| Parameter | Actual value |
|-----------|--------------|
| 1 Kinematic viscosity at 100 °C according to FS 33, mm²/sec | 4,67 |
| 2 Kinematic viscosity at 40 °C according to FS 33, mm²/sec | 17,8 |
| 3 Viscosity index according to FS 25371 | 197 |
| 4 Closed cup-flash point according to FS 6456, °C | 293 |
| 5 Acid number according to FS 5985, mg Cohn per 1 g oil | 163,7 |
| 6 Mass fraction of sulfur according to ASTM D 4284, % | 0,008 |
| 7 Density at 15 °C according to ASTM D 4052, g/cm³ | 0,918 |
| 8 Density at 20 °C according to ASTM D 4052, g/cm³ | 0,915 |

Table 2. Quality of coniferous TOFA.

| Parameter | Actual value |
|-----------|--------------|
| 1 Kinematic viscosity при 100 °C according to FS 33, mm²/sec | 4,0 |
| 2 Kinematic viscosity при 40 °C according to FS 33, mm²/sec | 16,1 |
| 3 Viscosity index according to FS 25371 | 153 |
| 4 Closed cup-flash point according to FS 6456, °C | 307 |
| 5 Acid number according to FS 5985, mg KON per 1 g oil | 180,7 |
| 6 Mass fraction of sulfur according to ASTM D 4284, % | 0,007 |
| 7 Density at 15 °C according to ASTM D 4052, g/cm³ | 0,914 |
| 8 Density at 20 °C according to ASTM D 4052, g/cm³ | 0,911 |

Mixed TOFA and TOFA produced from coniferous trees have different quality characteristics due to the unique composition of tree species. However, due to the fact that different tree species are used for sulfate cooking, mixed TOFA are the most common ones. Therefore, mixed TOFA were used as a raw material.

The IR-spectrometric analysis of mixed and coniferous fatty acids was carried out. The IR spectrum of mixed TOFA is shown in Figures 1 and 2 (1). Due to the complete identity of the spectra of mixed and coniferous TOFA, the IR spectrum of coniferous TOFA is presented under figure 2 only in Figure 2 in comparison with the esterification reaction product.

The TOFA used in the present study belong to the most common group of fatty acids consisting of unsaturated acids having 18 carbon atoms [8]. Fatty acids consist of linoleic, oleic and linolenic carboxylic acids. Liquid carboxylic acids are used as dimers (according to the hydrogen bond) [9][10]. In the spectra presented in Figure 1, peaks in the range from 1715 to 1680 correspond to unsaturated dimers of carboxylic acids. In the 1420-1200 cm⁻¹ range, intense absorption caused by deformation vibrations O-H and stretching vibrations C-O manifests itself.

The gas chromatography mass spectrometric analysis of the sample was conducted. The spectrum is shown in Figure 2.

Figure 4 denotes a peak corresponding to linoleic acid prevailing in the mixture, as well as a tail in the form of non-polluted substances, resin acids, etc. In the TOFA mixture, there are oleic acid (peak 1), palmitic acid (peak 2) and linolenic acid (peak 3). In order to determine the boiling point of TOFA, the mixture was separated according to boiling points under vacuum conditions (5 mm Hg) by the
method developed by the Central laboratory of Angarsk petrochemical company. The results are presented in Table 3.

![Figure 1. The IR spectrum of mixed TOFA.](image1)

![Figure 2. The mass spectrum of TOFA.](image2)

**Table 3. Fraction composition of TOFA.**

| ic  | 5%  | 10% | 20% | 30% | 40% | 50% | 60% | 70% | 80% | 90% | 95% | fc | Output, % |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----------|
| 366 | 368 | 369 | 370 | 370 | 371 | 371 | 371 | 372 | 373 | 374 | 376 | 99 | |

Having a wide range of substances in its composition, TOFA have a narrow range of boiling points which complicates and makes it unprofitable purification of the mixture.

2.2. **Reagent**

Butyl alcohol was used as a reagent, since it is known that the rate of esterification is the highest for primary alcohols [11]. Along with esters, water removed from the reaction zone together with unreacted n-butanol was used as an esterification reaction product. Due to the fact that n-butanol is partially soluble in water [12], the stage of unreacted alcohol extraction was excluded.

2.3. **Catalyst**
As a catalyst, three types of ion exchange resins (Lewatit K2629, Amberlite 15 WATT and Tokem-100) were used. They have the ability to ion exchange reactions due to the presence of special functional groups.

3. Experimental Section

The process is based on the esterification reaction in the liquid phase:

\[ C_{18}H_{34}O_2 + C_{5}H_{10}O_2 \underset{\text{cat.}}{\longrightarrow} C_{20}H_{36}O_2 + H_2O \]  \hspace{1cm} (1)

The esterification reaction of TOFA with n-butanol (1:3 mass ratio) was carried out at an atmospheric pressure and 100-115 °C during 110-130 minutes until the water release has stopped. Ion exchange resins of three types in the amount of 5% of the TOFA mass were used as catalysts. An intermediate product whose quality indicators are presented in Table 4 was produced. The low acid number (>0.05 mg KOH/g) indicates an almost complete conversion of acid into ester [13].

**Table 4. Parameters of the TOFA esterification product.**

| Parameter                                      | Value       |
|------------------------------------------------|-------------|
| 1 Density at 20 °C according to ASTM D 4052, g/cm³ | 0,900       |
| 2 Kinematic viscosity at 40 °C no FS 33, mm²/sec | 8,47        |
| 3 Kinematic viscosity at 100 °C according to FS 33, mm²/sec | 2,54        |
| 4 Viscosity index according to FS 25371          | 136         |
| 5 Closed cup-flash point according to FS 6456, °C | 130         |
| 6 Acid number according to FS 5985, mg KOH per 1 g oil | <0,05       |
| 7 Pour point according to FS 20287, °C          | -21         |

In Figure 3, figures 1 and 2 denote the spectra of mixed and coniferous TOFA. Figure 3 is the spectrum of intermediate butyl ether of TOFA. The change in the spectra in the range of 1300-1050 cm⁻¹ is due to oscillations with the participation of a C-O-C ethereal bond. This indicates the presence of esters in the mixture. The change and shift of peaks in the range of 1730-1715 is typical for dimers of esters. Due to the use of raw materials which are made from the TOFA mixture containing various impurities, the product has a number of impurities. This affects quality of the product which can be
observed when comparing the data in Tables 1 and 4. The fractional composition of the product was identified. The data are presented in Table 5.

| Fraction composition, °C, | ic 5% | 10% | 20% | 30% | 40% | 50% | 60% | 70% | 80% | 90% | 95% | fc | Output, % |
|---------------------------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----------|
| 383                       | 383   | 386 | 387 | 388 | 390 | 391 | 392 | 394 | 405 | 445 | 446 | 96 |          |

The fractional composition of the esterification reaction product has a narrow range of boiling points. However, starting from 80%, a significant jump in the boiling point can be observed. These can be esters of resin acids, but decoding results for the resulting mixture are being studied. Ester fractions were produced from the esterification reaction product under vacuum conditions (5 mm Hg). Their parameters are presented in Table 6 in comparison with 100% Motul 8100 ECO-lite 5W-20 engine oil with energy-saving properties.

| Parameter                   | TOFA butyl ether | Motul engine oil 8100 ECO-lite 5W-20 |
|-----------------------------|------------------|-------------------------------------|
| 1 Kinematic viscosity at 100 °C, mm²/sec | 2.3              | 8.5                                 |
| 2 Viscosity index           | 238              | 170                                 |
| 3 Pour point, °C            | -55              | -42                                 |
| 4 Density, kg/m³            | 985              | 847                                 |

4. Results and Discussion

Esters produced during the esterification of higher carboxylic acids and alcohols are applied as lubricants and raw materials for their production. They can be a basis for the production of energy-saving oils with low kinematic viscosity (Table 6). However, kinematic viscosity of TOFA butyl esters is extremely low. The kinematic viscosity can be increased in several ways. Pentanol or hexanol with a high molecular mass can be used as a reagent [14]. However, it will increase the cost of the process. The viscosity can be increased by adding functional groups (-Si, -P) by double bonds of carboxylic acid molecules in the TOFA mixture. The viscosity can be increased by using additives. However, the authors focused on structural manipulations with esters.

5. Summary and Conclusion

The fact that Angarsk plant produces a TOFA-based anti-wear additive Baikat speaks for the use of TOFA esters as lubricants. Fatty acids are mixed with bottoms of butyl alcohols. Thus, TOFA butyl esters are a modification of "Baikat". In addition, it is known that TOFA can be used as lubricants having good biological decomposition and non-toxicity properties [15].

Due to the reversibility of esterification for TOFA butyl esters and TOFA-based products, the presence of water is undesirable. It is known that about 1 kg of water is produced from 1 kg of fuel, most of which evaporates. Cold cylinder walls cause condensation. Another source of water is leaking from the engine cooling system when the cylinder head gaskets break, or cracks in the cylinder head or block [16].

It is necessary to identify risks of hydrolysis for TOFA butyl esters by testing the maximum amount of water for proper operation of the internal combustion engine.

In addition, TOFA oxidation at a room temperature is a problem which causes formation of low-molecular acids that accelerate metal corrosion processes [17]. Therefore, TOFA storage requirements should be developed and ways to prevent oxidation of raw materials should be suggested.
The solution is crucial for the production of energy-saving oils and TOFA-based additives.

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