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Esters of linear monounsaturated dicarboxylic acids for lubricants

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Dibasic esters constitute a viable segment of oleochemical- and petrochemical-based lipid products, such as adipates, phthalates, succinates, sebacates, and “dimer acids,” used in plasticizers, cosmetics, lubricants, paint thinners, colorant diluents, and other industrial oil products.

- **Esters of linear alpha,omega-dicarboxylic acids are used in high-performance hydraulic fluids.**
- **Despite poorer oxidative stability, monounsaturation provides many benefits.**
- **Mono-unsaturated diacids can be produced by metathesis or biocatalytically.**

Among larger-volume products, saturated dibasic esters of higher molecular weight are sometimes employed in high-performance hydraulic fluids, which require specified viscosities, good fluidity at low temperatures, resistance to aging, lubricity, and other more specialized properties. Currently, high-performance hydraulic fluids are dominated by sebacates and azelates, esters of C10:0 1,10-di-OOH and C9:0 1,9-di-OOH alpha,omega-dicarboxylic acids, respectively. Usually 2-ethyl hexanol or longer-chain petrochemical alcohols are used for esterification, producing viscosity grades of ISO VG22 and VG12 for niche applications. Sebacic acid is generally manufactured from castor oil, and its price is typically higher than that of commodity diacids such as adipic acid. In spite of this price disadvantage, petrochemical esters are widely used as basestocks for high-performance hydraulic fluids. Basestock is by far the dominant component in lubricant formulations; for hydraulic fluids it usually comprises over 95% wt.

Despite numerous efforts, biodegradable basestocks have not been incorporated into conventional internal combustion or diesel engine oils to any significant extent. In addition, current attempts to develop motor lubricants must consider the implications of electrical vehicles, which do not need traditional engine oils at all. Therefore, lubricant-oriented valorization of innovative basestocks is shifting toward hydraulic fluids, whose global market exceeds 10 million metric tons and includes products of quite diverse technical requirements.

Current advancements in green chemistry and bio-based technologies have given rise to new players among dibasic esters. High-temperature reactions over montmorillonite clay can produce a mix of methyl-branched C22 alpha,omega-dicarboxylic acids, which can be turned into dibasic esters [1]. For feedstock, 11-undecenoic acid is used, yielding trans double bonds. Unconventional raw materials and a complex purification procedure make this process difficult to scale up. Another pathway is presented by metathesis, which can also yield dibasic esters from oleate, erucate, and other unsaturated fatty acid (FA) esters, leading to a mixture of cis and trans isomers [2]. For this process, conventional monounsaturated FA or their esters can be used as feedstock. Biocatalytical pathways are also available to afford longer chain alpha,omega-dicarboxylic acids from these raw materials [3], yielding mostly cis isomers (Fig. 1).

The scenarios in Fig. 1 initially lead to unsaturated dibasic esters dominated by monounsaturation, which can be hydrogenated into saturated ones, if necessary. The lubricant industry is cautious about using unsaturated basestocks because of the higher probability of oxidative degradation. Nevertheless, many commercially successful hydraulic fluids use rapeseed, canola, and other vegetable oils as their basestocks, which comprise more than 20% mol. methylene-interrupted polyunsaturated FA. A well-formulated antioxidant package can inhibit oxidative degradation effectively in hydraulic fluids based on such vegetable oils, assuring excellent performance. Consequently, while medium iodine values in basestocks raise some concerns, highly monounsaturated dibasic esters remain strong candidates for high-performance hydraulic fluids.

Compared to mineral oil and petrochemical basestocks, dibasic esters offer several benefits for hydraulic fluids. They can be produced from renewable resources and appear to be easily biodegradable. They demonstrate high thermal conductivity, which results in lower operating temperatures and subsequent advantages in hydraulic systems. The volatility and flash points of dibasic esters are lower than those of petrochemical basestocks from the same viscosity grade. Their heat-thinning is not as rapid, and their inherent lubricity is considered to be better. Such advantages depend both on ester functionalities and monounsaturation, and it must be noted that they are often based on user experience, without much substantiation from research findings. Therefore, to better understand the impact of molecular factors on the properties of dibasic esters, each parameter must be assessed more thoroughly.

HEAT-THINNING OF UNSATURATED ESTERS

Operational viscosity is very important in hydraulic systems. Viscosity grades of hydraulic fluids are determined at 40°C, which is a very approximate average temperature in a hydraulic system. When designing pumps and other components, viscosity's dependence on temperature is always accounted for,

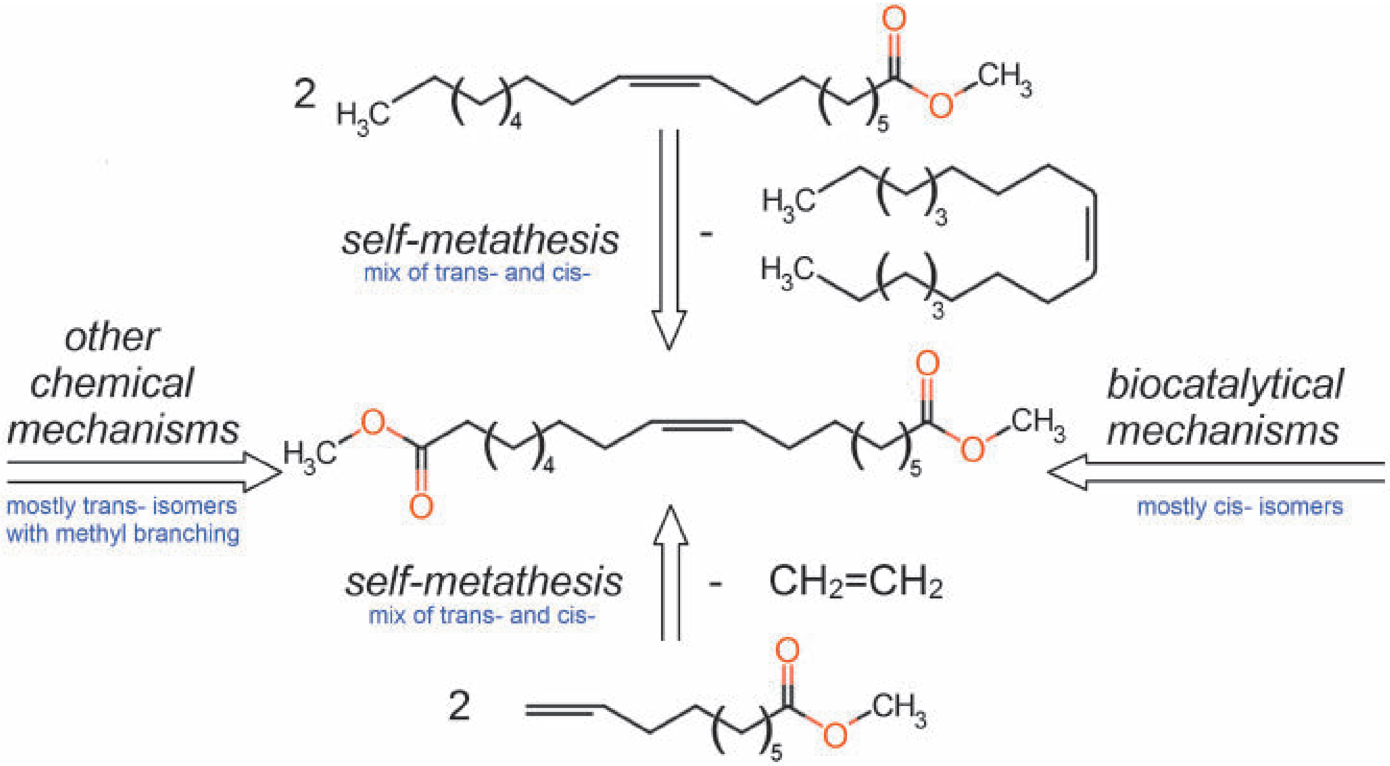

FIG. 1. Synthetic pathways to obtain monounsaturated linear alpha,omega-dibasic esters with the dominant isomers listed in parenthesis for each process

but performance can still be strongly affected by viscosity variations. Multiple studies report that the best energy efficiency and overall performance are achieved when heat-thinning is as low as possible. For example, in winter, hydraulic equipment must be turned on when the weather is very cold. In summer, when the equipment operates continuously, hydraulic fluid often reaches 90°C or higher. In lubricant technology, heat-thinning is assessed by the Viscosity Index (VI), which is determined by measuring kinematic viscosities at 40°C and 100°C or two similar temperatures. For example, squalane, which is often compared to a typical molecule of conventional lubricants, has kinematic viscosities of 20.9 and 4.2 mm²/s at 40°C and 100°C, respectively, producing a VI of 103.

Most mineral oil basestocks have a VI below 100, while poly alpha olefins, a dominant synthetic basestock, have a VI of about 130. Fluids with high VI undergo less heat-thinning. Polymer additives are used to improve the VI of many lubricants, because in the friction zone temperatures are much higher than in bulk lubricants, and oil remains more viscous in the asperity contact. Consequently, surfaces are better separated, less metal-to-metal contact takes place, and wear is reduced. However, in hydraulic fluids, VI-improver polymers are exposed to extensive mechanical shear, which frequently reduces their VI to the vicinity of the basestock values.

Dibasic esters have significant advantages when it comes to VI, especially if they approach linear molecular structure. Di 2-ethylhexyl ("di-2EH") ester of azelaic acid shows just a medium VI = 97 because of its two ethyl branches. However, di-2EH ester of C18:0 saturated dibasic acid approaches VI 190 due to its more linear molecular architecture (Table 1). Unsaturation is another molecular factor that boosts VI, especially cis-double bonds. This is very obvious when comparing vegetable oils; rapeseed oil has a VI of 222, while soybean oil, which is less saturated, hits VI = 246. Dibasic esters show similar effects, with di-2EH ester of C18:1 dibasic acid (mostly trans-) achieving VI = 197.

Monounsaturated esters of linear long-chain dibasic acids approach VI of rapeseed oil. For hydraulic equipment, which operates at higher temperatures, rapeseed oil viscosity might be higher than that of a VG46 fluid of VI=100, which records 6.8 mm²/s at 100°C. Dibasic esters can provide a closer alternative to design specifications with a number of other benefits.

LOW TEMPERATURE FLUIDITY

In hydraulic fluids, good performance at low temperatures is often required, depending on climatic conditions. The first measure used to describe cold fluidity is usually the pour point, the point when fluid chilled at a prescribed rate of 0.3 to 3°C/min stops pouring out of a test tube when periodically inverted. As seen in Table 1, dibasic esters of C12:0 or shorter chains perform very well at low temperatures. Monounsaturation is very helpful for C18 dibasic esters, even despite predominant trans isomerization. In aviation, forestry, and some other fields, cold performance might be among the top criteria for hydraulic fluids.

THERMAL CONDUCTIVITY OF ESTERS

The higher thermal conductivity of esters relative to hydrocarbons can help reduce the temperature of a hydraulic system. Thermal conductivities of vegetable oils, which are about 167 mW/(m·K) at 20°C are nearly a quarter higher than those of mineral oils, which are about 133 mW/(m·K). Other esters have been recorded to have similar thermal conductivities, while those of dibasic esters are not very well established. Some data shows that unsaturation might also be beneficial towards thermal conductivity, but more tests are needed to correlate it to the number of double bonds.

WEAR-REDUCTION BY UNSATURATED DIBASIC ESTERS

Hydraulic fluids prevent pumps from wearing too much under normal operating conditions by forming protective tribofilms on friction zone surfaces. These protective films must be constantly replenished by hydraulic fluid components to prevent metal from wear. Ideally, basestocks should contribute to tribofilm formation. In saturated basestocks, friction zone temperatures must be quite high to ensure that effective tribofilms are formed. Anti-wear additives must be formulated carefully. Since double bonds are considered to be at least 10 times more reactive chemically, their contribution to tribofilm formation should be much higher. In addition, ester monolayers can saponify to form soaps on metal surfaces, which can enhance the protective effects of tribofilms. More studies are needed, but it seems that unsaturated dibasic esters might provide better wear-reduction

TABLE 1. Viscosity and Viscosity Index (VI) of commercial basestocks and reported di-(2-ethylhexyl) esters of di-OOH alpha,omega-dicarboxylic acids; e.g., alpha-omega 9:0; i.e., azelaic a.

Basestock	mm²/s 40°C	mm²/s 100°C	VI	pour pt °C
Paraffinic mineral oil	46	6.8	100	-12
Poly alpha olefin	50.5	8.2	135	<-66
Rapeseed oil	46.8	10.7	222	-24
di-2EH of azelaic a.	10.5	2.7	97	-57
di-2EH of α-ω 12:0	14.7	3.7	145	-48
di-2EH of α-ω 18:0	23.9	5.7	194	-9
di-2EH of α-ω 18:1	22.4	5.5	197	-57
di-2EH of α-ω 20:0	29.0	6.5	190	-3

with lower concentrations of anti-wear additives. This is especially beneficial to hydraulic fluids, which have a long service life in which additive depletion is a major issue.

Our research indicates that monounsaturated dibasic esters of linear alpha,omega-dicarboxylic acids have very good potential as basestocks for high-performance hydraulic fluids. Their heat-thinning is much slower, which is very beneficial for hydraulic systems. Thermal conductivity is significantly higher, resulting in energy savings and much lower operating temperatures. Oxidative stability can be balanced with antioxidants, while wear can be reduced more easily than in saturated basestocks. Other properties, including low temperature fluidity, should also meet high-performance requirements. Therefore, synthesis and testing efforts in this direction can result in new industrial oil products of significant potential volumes.

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