Evaluating Base Oil Alternatives: Esters, PAGs, and Olefins

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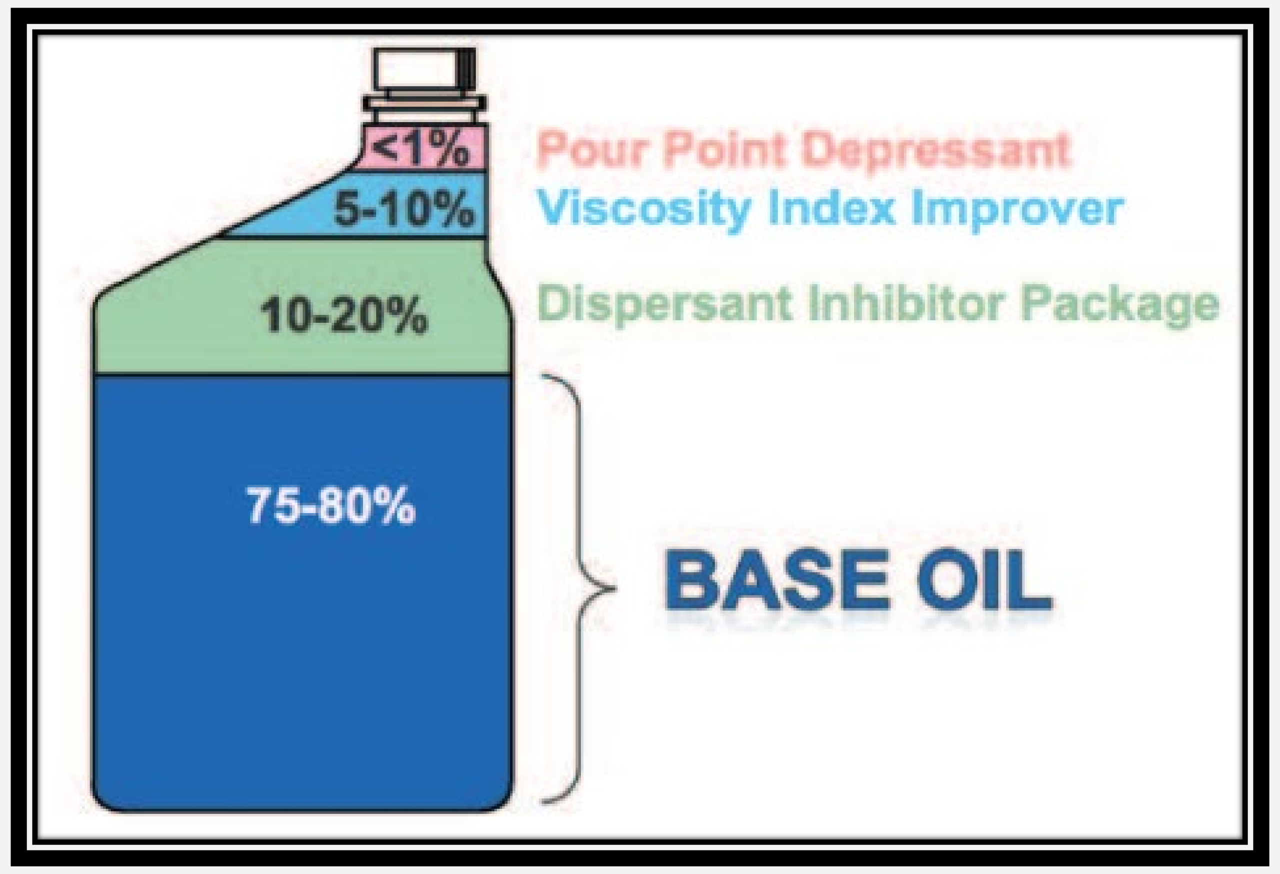
Overview

- The constant evolution of automobiles and emissions regulations places a need for constant innovation of engine oil formulations
- Growing needs for lower viscosities and improved friction properties at wider operating boundaries will require an alternative to traditional petroleum base oils
- Alternative base oils present an opportunity to improve fuel economy and performance necessary for next generation engines

Base Oil: Definition

A base oil can be considered as one of the fundamental ingredients that make up all engine oils and lubricant formulations. For engine oils, the base oil makes up around 75% to 80% of an engine oil, which is the vast majority of the product. The figure below shows the typical percentages of the ingredients used to make engine oil. Base oils are typically produced by refining crude oil and are categorized by the API into groups I-V with increasing levels of refinement. Groups I-III are traditional base oils refined from crude oil with increasing levels of refinement and lubricating properties. Group IV consists of polyalphaolefins (PAOs) and represent a class of synthetic lubricants while Group V encompasses any other base oils that don't fit into the previous groups such as esters, polyalkylene glycol (PAG), and bio-olefins. Outside of the API definition, a group VI exists in Europe for polyinternal olefins as classified by the ATIEL.



Typical Non-Petroleum Based Base Oils

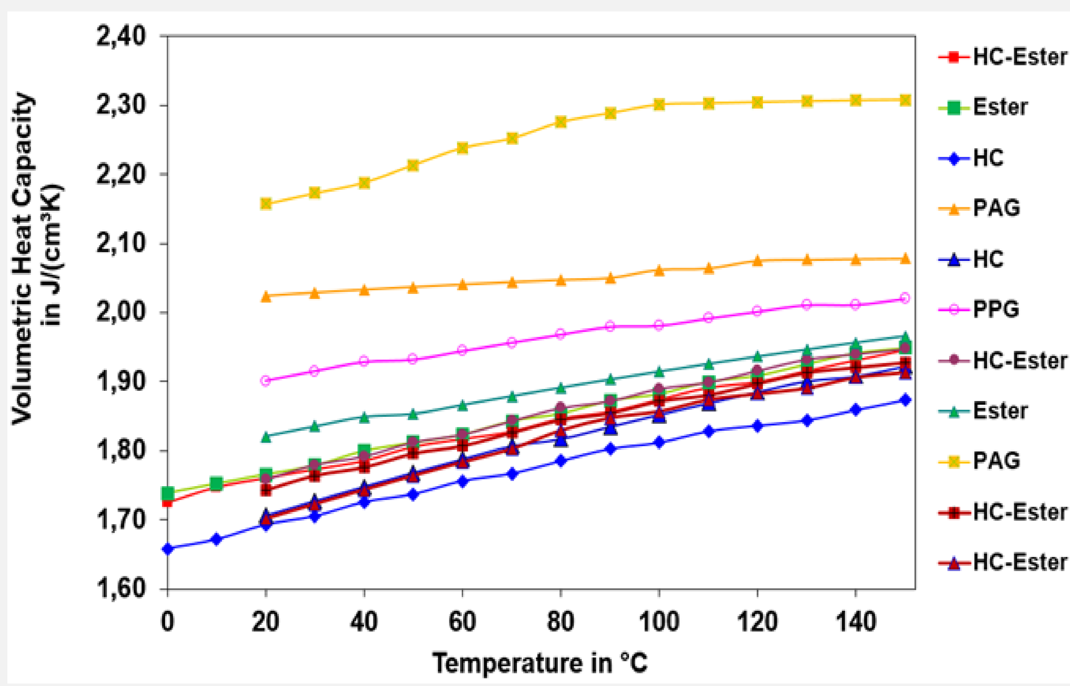
Although the majority of base oil is derived from crude oil, the alternative base oils that fall within the higher API base oil groups IV and V possess a number of properties that often exceed that of their crude oil derived counterparts. As such numerous alternatives base oils derived from these higher groups such as bio-olefins, esters, and PAGs, are being investigated for their numerous advantages. The table below summarizes common strengths and weaknesses of the classes of common alternative base oils. These typically consider biodegradability, viscosity index (VI), oxidative stability, volatility, wear resistance, and lubricity for engine oils. Many Group V base oils listed on the table are being investigated recently due to their capabilities in lower viscosity/friction engine oils. Esters and PAGs in particular have much lower NOACK evaporation/volatility at low viscosities due to their molecular polarity inherent to their molecular structure.

Common Alternative Base Oil Properties

Synthetic	Strengths	Weaknesses
Polyalphaolefins (PAOs) Maximum Operating Temperature 399°F/ up to 204°C	High VI, high thermal oxidative stability, low volatility, good flow properties at low temperatures, nontoxic and compatible with mineral oils	Biodegradability depends on molar mass, limited additive solubility, seal shrinkage risk
Di-, tri-, tetraesters and Polyolesters Temperature 399°F / up to 204°C	Nontoxic and biodegradable, high VI, good low-temperature properties, miscible with hydrocarbons	Hydrolytic stability and miscibility with hydrocarbons can be an issue, limited seal and paint compatibility
Phosphate Esters Maximum Operating Temperature 241°F/116°C	Highest auto-ignition temperature, excellent wear resistance and scuffing protection	Moderate VI, limited seal compatibility, not miscible with hydrocarbons, moderate hydrolytic stability
Polyalkylene Glycols (PAGs) Temperature 399°F / up to 204°C	Low friction and excellent lubricity, nontoxic and biodegradable, high VI, good thermal and oxidative stability	Limitations in soluble additives, miscibility with other base oils depends on backbone, limited seal and paint compatibility
Silicones Maximum Operating Temperature 486°F/252°C	Highest VI, high chemical stability, excellent seal compatibility, very good thermal and oxidative stability	Not miscible with hydrocarbons and additives, weak lubricity under mixed/boundary lubrication

Advantages of Esters and PAGs

Heat Capacity Comparison of Esters and PAG with Traditional Base Oils and Blends



Esters and PAGs both possess an oxygen atom within their carbon backbone that gives them unique advantages over traditional hydrocarbon base oils. The additional polarity caused by the presence of the oxygen atom improves lubricity, viscosity index, and reduces NOACK evaporation but simultaneously reduces compatibility with polymeric materials used in additive packages. Esters in particular have strong viscosity index, thermal/oxidative stabilities, and reduced NOACK volatility which has made them promising for high temperature low viscosity engine oils but may suffer from thermal degradation. They also are capable of qualifying as an environmentally acceptable lubricant (EAL) as per the US Vessel General Permit. PAG's on the other hand, possess similar characteristics such as high lubricity, high viscosity index, and low NOACK evaporation, but possess uniquely high heat capacities over both esters and hydrocarbons as shown in the figure above that make them suitable for high temperature low viscosity engine oils with greater viscosity retention and film-forming abilities to reduce wear. They are also more capable of blending with other base oils/formulations due to their capability of being water and oil-soluble allowing for greater flexibility in engine oil applications and easier maintenance/cleaning.

Oil-Soluble PAGs and Bio-Olefins

Unique Properties of OSPs

Quantity	Method ASTM	OSP -18	OSP -32	OSP -46	OSP -68	OSP -150	OSP -220	OSP -320	OSP -460	OSP -680
Kin. Viscosity at 40°C [mm²/sec]	D445	18	32	46	68	150	220	320	460	**680**
Kin. viscosity at 100°C [mm²/sec]	D445	4.0	6.4	8.5	11.5	23.5	33	36	52	**77**
Viscosity Index	D445	123	146	164	166	188	196	163	177	**196**
Pour point [°C]	D97	-41	-57	-57	-53	-37	-34	-37	-35	**-30**
Fire point [°C]	D92	220	242	240	258	258	258	260	265	**270**
Density at 25°C [g/ml]	D7042	0.92	0.94	0.97	0.97	0.97	0.97	0.97	0.97	**0.97**
Aniline point [°C]	**D611**	**<-30**	**<-30**	**<-30**	**<-30**	**<-30**	**-26**	**n/d**	**n/d**	**n/d**

A sub-class of PAGs known as oil-soluble PAGs (OSPs) possess the advantages of PAGs but with significantly greater flexibility in formulation that allows for a wide range of operating applications as shown in the table to the left. Bio-olefins possess a similar aspect but in their feedstocks as bio-olefins can be produced from a wide array of biomass feedstocks. Through processes such as fermentation, gasification, etc., green algae and sugar from yeast cells can be converted into useful oxygenates/olefins such as ethylene that possess similar advantages as PAGs and Esters.

Conclusion

- Alternative base oils can improve fuel economy and performance as they can leave the engine oil cleaner for much longer compared to the traditional engine oil and reduce the material footprint.
- This increases vehicle mileage and allows the vehicle to reduce CO_2 emissions without having to replace the engine.
- In the near future, it can be expected that there will be more lubricant formulas that incorporate alternative base oils.

References

- Lee, David. Base Oil Basics: Quality Starts at the Base. Chevron Lubricants, 1 Feb. 2018
- "Modern Base Oils & Blending for Optimal Performance." Lube-Tech, Feb. 2012, pp. 1–7.
- "Base Oil Groups Explained." Machinery Lubrication, Noria Corporation, 9 Oct. 2012
- "Hydrocracking." Hydrocracking - an Overview, ScienceDirect Topics, 2019,
- Fitch, Bennett. "Understanding the Differences Between Base Oil Formulations." Machinery Lubrication, 6 Feb. 2017,
- Esche, C., et al. Esters for Engine Oils. Tribology and Lubrication Technology, November 2018, p. 80-82.
- Standard Guide for Selection of Environmentally Acceptable Lubricants for the U.S. Environmental Protection Agency (EPA) Vessel General Permit, ASTM work item WK68688
- M.R. Greaves, Oil Soluble Polyalkylene glycols, in: Rudnick, L.R. (ed), Synthetics, Mineral Oils and Biobased Lubricants
- Woydt, Mathias. Polyalkylene Glycols as Next Generation Engine Oils, Journal of ASTM International, Vol. 8, No. 6, paper ID JAI103368 and ASTM STP1521, 2012, ISBN: 978-0-8031-7507-5
- R. Schmidt, G. Klingenberg and M. Woydt, Thermophysical and viscosimetric properties of environmentally acceptable lubricants, Industrial Lubrication and Tribology, 2006, Vol. 58, issue 4, p. 210-224
- Greaves, Martin. "Oil Soluble Polyalkylene Glycols". LUBE-Tech, Dec. 2013, pp. 1–4.
- V. Zacharopoulou and A.A. Lemonidou, Olefins from Biomass Intermediates: A Review, *Catalysts* 2018, *8*(1), 2; https://doi.org/10.3390/catal8010002

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