The resurgence of polyalkylene glycols (PAGs) for hydrogen combustion engines

***Dr. Mathias Woydt**, Managing Partner, MATRILUB, Berlin*

All "green" technologies require certain resources or minerals being either scarce or monopolised. The International Energy Agency concluded in its latest report [1], that the large quantities consumed by "green" technologies will limit their market penetration. In this respect, for CO_2-neutral or low-CO_2 mobility, the internal combustion of hydrogen must be taken into account in addition to its use in fuel cells.

The BMW Hydrogen 7 V12 Clean Energy and the MAZDA RX-8 Hydrogen RE (Wankel-type) were highly developed vehicles in the 2000s. Recently, interest has rekindled in commercial vehicles, such as M.A.N. and CUMMINS, with a first TOYOTA Corolla with a hydrogen fuel engine (3-cyl., 1.6 L Turbo) making its rounds on a race track in Japan in 2021.

The industrialisation of polyglycols began in the late 1920s with Union Carbide (US 1,633,927) and I.G. Farben (US 1,921,378). From March 1944 to August 1945, the U.S. Air Force accumulated more than 200,000 flight hours in the P-38, P-47, P-51 and B-25 aircraft [2]. The following observations were made: cold start at -40°C possible, no sludge formation and sludge-free oil coolers, no deposits on pistons, extended oil change intervals, clean engines. If it flies safely, then it can also drive on the road

In 1973, ELF developed the brand "13,000 tours" or "HVS529" (Huiles pour Voitures de Sports, SAE 15W-50) for Renault [3] with a fully formulated polyglycol-based engine oil (see Figure 1). Over the following decades, Formula 1 racing teams repeatedly used PAGs. At that time, the functional profile of polyglycols in combinations with open questions about miscibility with hydrocarbons and seal compatibility did not justify the additional costs. The structure-properties relationships between a polyglycol formulations and elastomers are well understood today.

***Fig. 1:** Photos of the containers of the ELF 13000 Tours (design of the containers: Roger Tallon)*

Since the mid-1990s, the development of polyglycol-based engine oils has been driven forward by automotive OEMs in the sense of a metal-, ash- and polymer-free strategy (FR 2,792,325, US 6,194,359, DE 10 2005 011,776, US 8,357,644) [4.5]. The motivations were derived from efforts to reduce fuel consumption and because the engine oil should not have a negative impact on the durability of particulate filters and catalysers [6]. The formulations used there also met the criteria for environmentally friendly lubricants and bio-lubricants.

Lubricant products based on polyglycols cover the entire range of applications, although they only have market shares in certain areas. Traditionally, PAGs are used in flame-retardant hydraulic oils. Furthermore, there are homologated applications in gas turbines and gearboxes in wind turbines, such as in particular in worm and industrial gearboxes as well as compressors and metal working fluids. Heat transfer fluids and as lubes in air conditioning systems as well as well drilling fluid represent further applications.

Entry in Water

Engine oils on hydrocarbon and/or ester bases suffer from the consequences of water inputs in lubricants that are produced during the combustion of hydrogen and are inevitably introduced into the crankcase, which shortens their oil change intervals. This requires a base oil with intrinsic water solubility. Polyalkylene glycols depict these water-dissolving to water-soluble properties. Water in the lubricant, whether dissolved or dispersed, promotes corrosion, taking into account that this circumstance is well solved by additives in water-based metalworking fluids and fire resistant hydraulic oils and this knowledge also exists for PAG-based engine oils. PAGs are naturally hydrolysis resistant. Compared to a dispersion of water, the corrosion potential is reduced by the dissolution of the water in PAGs, but still present.

It should also be emphasised that PAGs have an exceptional viscosity tolerance to water inputs of up to 40 % and practically no viscosity drop occurs up to an input of 10 % water.

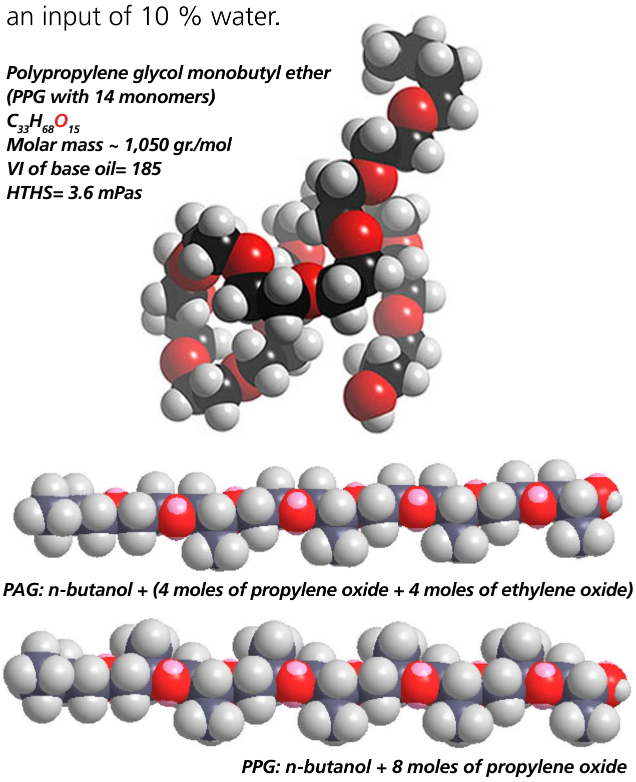

Fig. 2: *Illustrations of common PAG molecules (red: oxygen atoms)*

Tests with spherical roller bearings have shown that their service life at PAG in ISO VG220 with 2% water compared to mineral oil and PAO is significantly longer [7]. In a two-year field trial in 2 MW onshore wind turbines with planetary gearboxes, the viscosity of a PAG in ISO 320 remained stable (< ±7%) and the content of abrasive metals below 20 ppm [8].

Structure of PAGs

PAGs are all petrochemical, synthetic lubricants and this also explains the price level above mineral oils. PAGs are polymerised from "single building blocks" or monomers (see Figure 2).

The oxygen present in each monomer of the main chain of PAGs determines its intrinsic properties as a base oil, such as high viscosity indices, low NOACK evaporation, soot-free combustion, very good extreme pressure properties, high heat capacities, etc., enabling metal-, ash- and polymer-free engine oil formulations that support the functional advantages, such as improved fuel savings or no adverse effects on exhaust gas after-treatment devices.

The oxygen polarities define the intrinsic water solubility, which ranges from a complete water solubility of polyethylene glycols (PEG) or most polyalkylene glycols to the water-dissolving properties of polypropylene glycols (PPG).

Friction reduction through PAGs

Friction reductions in every mechanical application mean savings in drive energy or reduced energy/fuel consumption or longer ranges. Polyglycol-based formulations showed more or less the lowest friction losses in virtually every historical benchmark on the lubricity of various base oil compounds in highly concentrated rolling contacts and in engines (see Figure 3).

This is mainly due to the oxygen polarity in each monomer, which promotes adsorption on surfaces and thus reduces the coefficients of friction under mixing/boundary lubrication. Depending on the molecular structure and viscosity grade, the latter being proportional to the molecular weight, move the viscosity indices of the base oils between 170 and 250. Consequently, viscosity index improvers are no longer needed. The flat viscosity temperature curves derive the fuel economy advantages at cold start and low oil temperatures as well as under transient driving/usage profiles. The fuel economy saving is thus achieved by their viscometric and low friction properties [9].

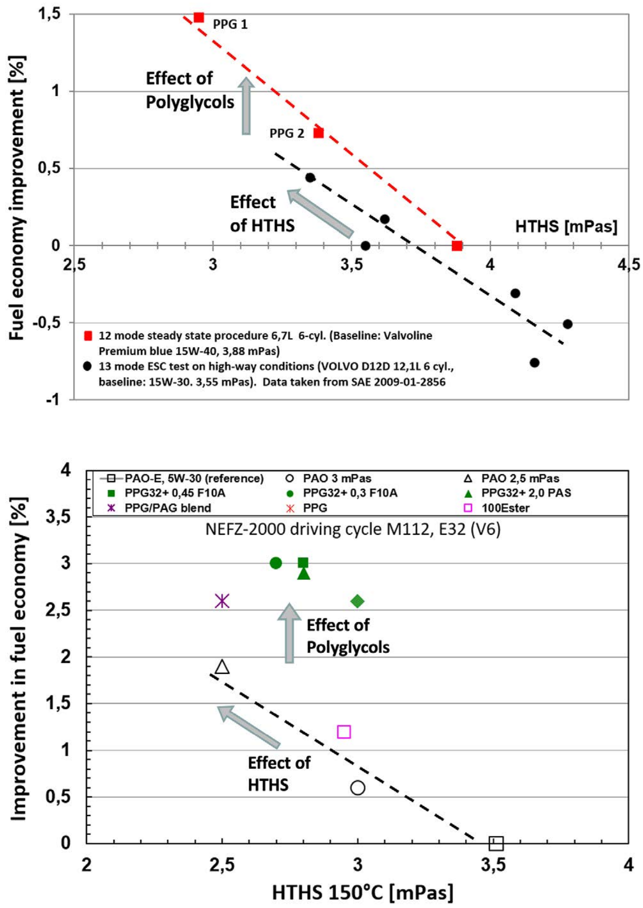

Fig. 3: *Effect of high-temperature high shear viscosity (HTHS) and polyglycols on fuel economy (data: top for trucks in [10]; bottom for passenger cars from DE 10 2005 011 776)*

Thermal management

Water offers the highest heat capacity, either by weight or volume, and also the highest thermal conductivity of fluids followed for both properties by polyglycols for anhydrous fluid. PAGs control better by their enhanced heat capacity and thermal diffusivity [11] the oil film thickness in the tribo-contact, because they can dissipate 10-20% more heat, which transduce in lower oil film temperatures with a better retention of oil film thickness. This favors the use of lower viscosity grades without loosing wear protection in terms of oil film thicknesses.

Biogenic Raw Materials

Sustainability requirements are increasingly in demand and shape product development. Today, the most common building blocks of PAGs, such as n-butanol, ethylene oxide and propylene oxide, can be obtained from renewable raw materials or biogenic resources. Bio-butanol is marketable as well as bio-ethylene oxide derived from bio-ethanol. For bio-propylene oxide, biogenic glycerine is recommended from bio-Diesel production. Thus, PAGs are also sufficient for sustainability and promote the circular economy. Consequently, they then have a favorable CO_2 emission factor.

The first PAG varieties from biogenic resources were recently offered on the market. PAG-based formulations can meet the bio-no-tox criteria of environmentally friendly lubricants.

Availability

The large-scale plant capacities of the PAGs exceed the availability of the esters and the PAGs meet all future quantity attributes for motor and transmission oils and are worth reviving in terms of their functional profile. The known, global production volumes (resource availability) of ethylene oxide (2019: ~30 million tonnes) and propylene oxide (2019: ~11 million tonnes) together with those of n-butanol may serve as orientation here.

References

[1] The Role of Critical Minerals in Clean Energy Transition – World Energy Outlook Special Report- Minerals in Clean Energy Transitions, May 2021, https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions

[2] C. Kratzer, D. H. Green and D. B. Williams, New synthetic lubricants, SAE Journal (Transactions), vol. 54, No. 5, May, 1946, p. 228–238

[3] N. N., Délai de réflexion avant lancement, Équipe, 07./08. April 1973, p. 12 and „Une nouvelle huile de synthèse: l'ELF 13000 tours", idem, 23. February 1973

[4] A. Gangopadhyay et al., Engine Friction and Wear Performances with Polyalkylene Glycol Engine Oils, SAE Technical Paper 2016-01-2271, 2016, doi:10.4271/2016-01- 2271

[5] L. Girard, S. Tung, M. Woydt, D. Bachelder, AUTOMOTIVE ENGINE LUBRICANTS, In: ASTM MNL37 Fuels and Lubricants Handbook, 2019, Chapter 20, p. 753– 864, ISBN-13: 978-0-8031-7089-6

[6] M. Woydt, No/Low SAP and Alternative Engine Oil Development and Testing, J. of ASTM Int., 2007, Vol. 4, No. 10, online ISSN 1546-962X or in ASTM STP 1501 "Automotive Lubricants – Testing and Additive Development", ISBN 978-0-8031-4505-4, eds.: Tung/Kinker/Woydt

[7] D. Brenner und J. Witzig, Zulässiger Wassergehalt in Getriebeschmierölen, insbesondere Polyglykol-Ölen und der Einfluss auf die Wälzlagerlebensdauer und die Zahnflankentragfähigkeit einsatzgehärteter Stirnräder, FVA-Informationsblatt zum Forschungsvorhaben 488 «Wassergehalt in Ölen», 09.02.2009

[8] H. Møller, Lubrication selection for the Horns Reef project, 14th Colloquium Tribology „Lubricants, Materials and Lubrication Engineering“, 13.-15. January 2004, Vol. II, p. 1241–1245, ISBN 3-924813-54-x

[9] M. Woydt, Polyglycols as Engine Oils, In: Encyclopedia of Lubricants and Lubrication; Ed.: Theo Mang, Springer, 2014, ISBN 978-3-642-22646-5

[10] S. Merryweather, D. Zweifel and M. Woydt, Polyglycol-based engine oils – Has the industry to adapt to this lubricant class?, Proc. 5th World Tribology Conference, Torino, Italy, September 8–13, 2013, ISBN 978-88-908185

[11] 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, https://doi.org/10.1108/00368790610670809

Dr. Mathias Woydt

Dr. Mathias Woydt is managing partner of MATRILUB Materials | Tribology | Lubrication, with 36 years of professional experience in tribology, lubrication technology and materials science. He is a recipient of the ASTM Award of Excellence and STLE Fellow as well as a member of the board of Ges. f. Tribologie e. V.