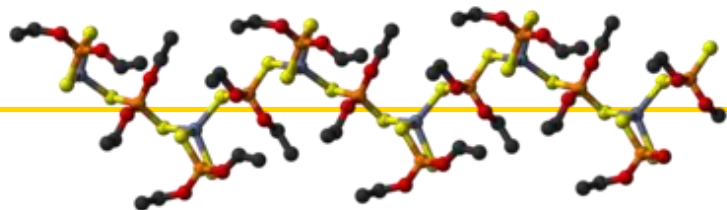


New alternative components to replace ZDDP

ZDDP - Zinc DialkylDithioPhosphates



Why ZDDP is so important in the lubrication?

Since **1944**, when **Mr. H. Freuler** patented the use of ZDDP in lubrication systems, no other component has been able to replace it.

ZDDP has the ability to simultaneously function as an excellent **antiwear agent**, a **mild extreme-pressure (EP) agent**, and an **effective oxidation and corrosion inhibitor**

Can we manufacture a lubricant without ZDDP?

Let's see...

Eni R&D activity on additives

Study and development of new additives based on new performance requirements, business requests and specific customer requests

Technical support to the production and marketing of additives

- Support to the improvement of Robassomero production processes
- Prevention and resolution of product quality problems
- Technical support to new potential customer

Identification and evaluation of alternative raw materials for the production of component and additive packages with cost reduction and quality maintenance



Development of new automotive lubricants

Friction reduction

Lubricating oil plays an important role in reducing friction losses

- Reduction of oil viscosity
- Use of Friction Reducer Additives

Low impact on aftertreatment

Vehicles equipped with exhaust gas treatment devices to reduce emissions and minimise

- Phosphorus contained in the oil poisons catalytic converters
- Sulfur deactivates the catalytic converters (reversible)
- Organometallic additives have the tendency to clog the DPF

Engine protection and durability

Low-speed pre-ignition (LSPI) is a phenomena in downsized, direct injection and turbocharged gasoline engines designed for high fuel economy

This phenomena is influenced by additives: Ca detergents can promote LSPI

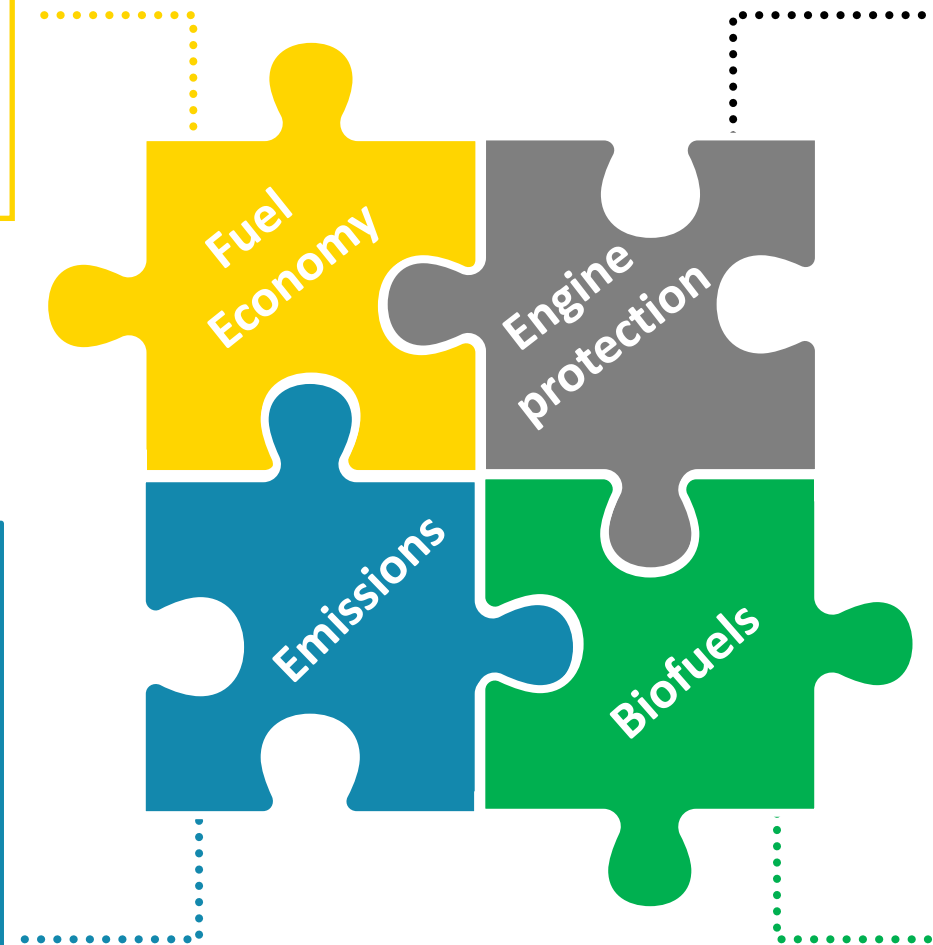
Optimization of the additive system to avoid possible damages to the engine

High tolerance

Unburned biofuel (e.g biodiesel) condenses on cylinder wall and is pushed down by oil rings into the sump, contaminating the lubricant

Use of efficient antioxidants and corrosion inhibitors in order to

- Decrease of viscosity and stability
- Increase of corrosion phenomena
- Possible presence of water in the sump

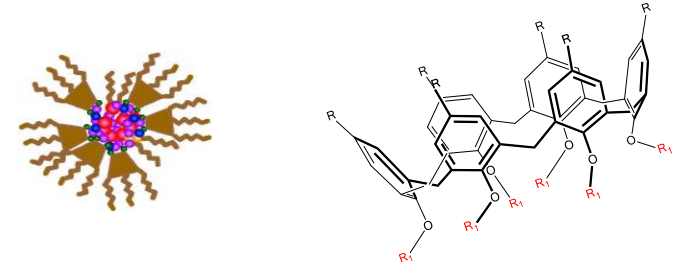


Can we do without ZDDP?... What's new in Eni



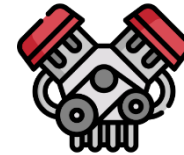
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Calixarene based detergents



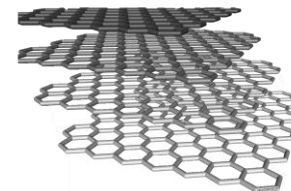
2

Organic bio-based friction reducers



3

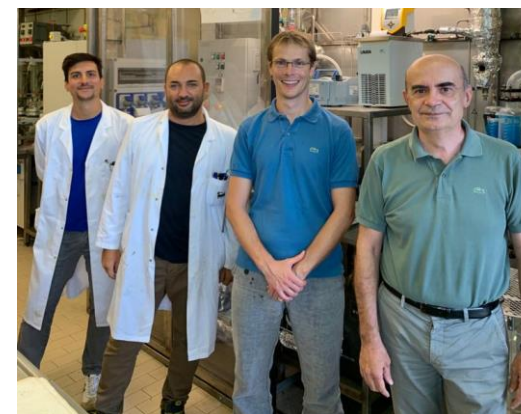
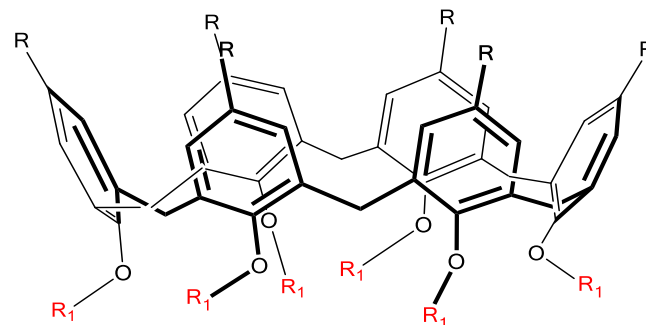
Nano-Additives for friction and wear reduction



Eni research on additives – New detergents

To meet the emerging needs, Eni, in collaboration with the *University of Parma* has developed
new detergents sulfur free based on calcium salts of calixarenes

Calixarenes



Calixarene based detergent applications

APPLICATIONS

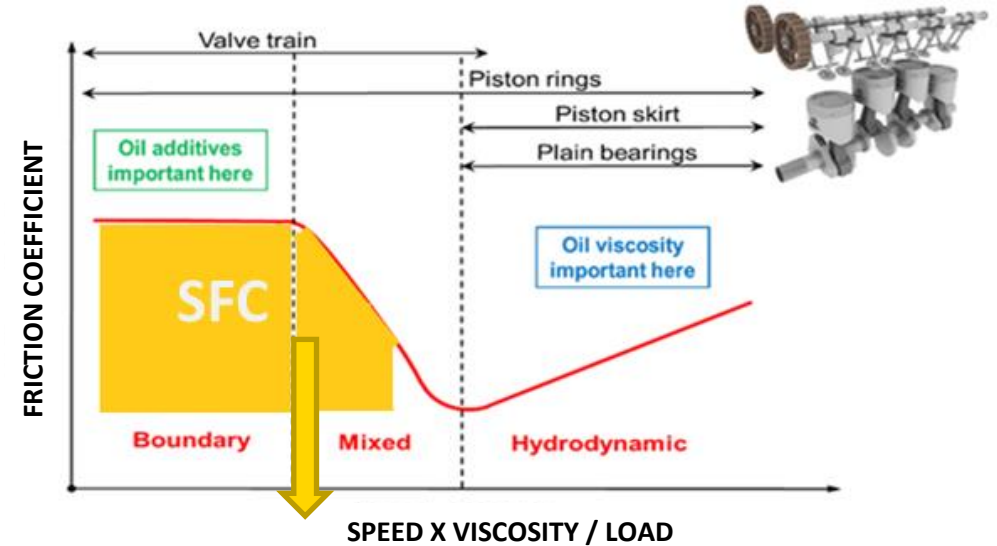
Automotive use



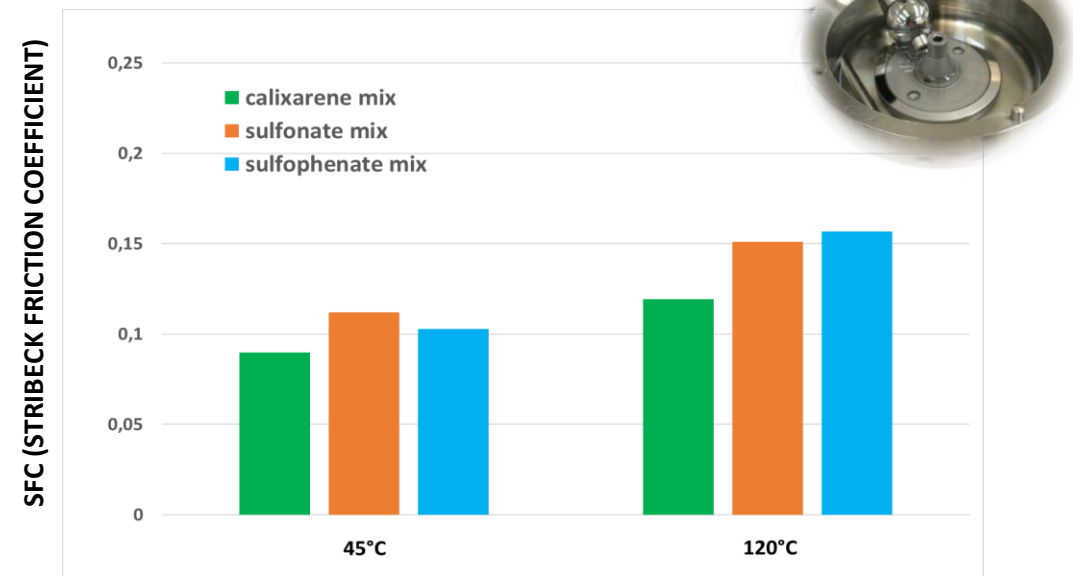
Marine use

- **Excellent detergency** → meet the targets of Marine OEMs
- **Sulfur free** → suitable for high performance Low SAPS engine oils
- **Proven friction reduction behaviour** → improve engine Fuel Economy

STRIBECK CURVE: LUBRICATION REGIMES



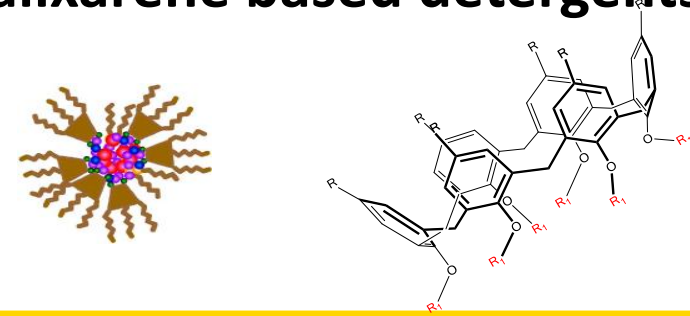
MINI TRACTION MACHINE TEST



Can we do without ZDDP?... What's new in Eni

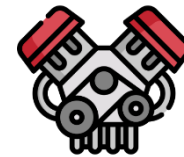
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Calixarene based detergents



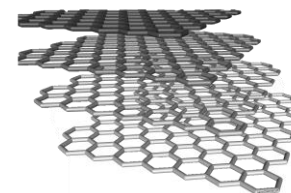
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Organic bio-based friction reducers

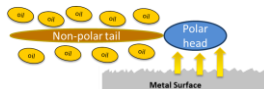


3

Nano-Additives for friction and wear reduction



Friction Reducers



100%



Lubricants are fundamental in the reduction of the friction loss

15%

Used "to move"

Energy used for effective motion

25%

Energy losses

15% Idling
10% Auxiliary systems

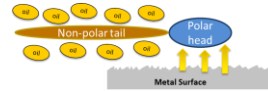
60%

Energy losses

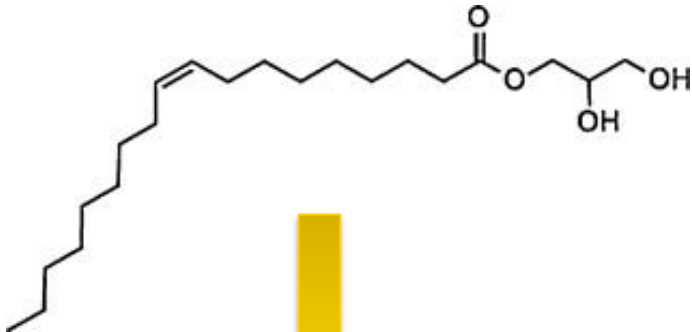
40% Heat ICE
20 % Friction



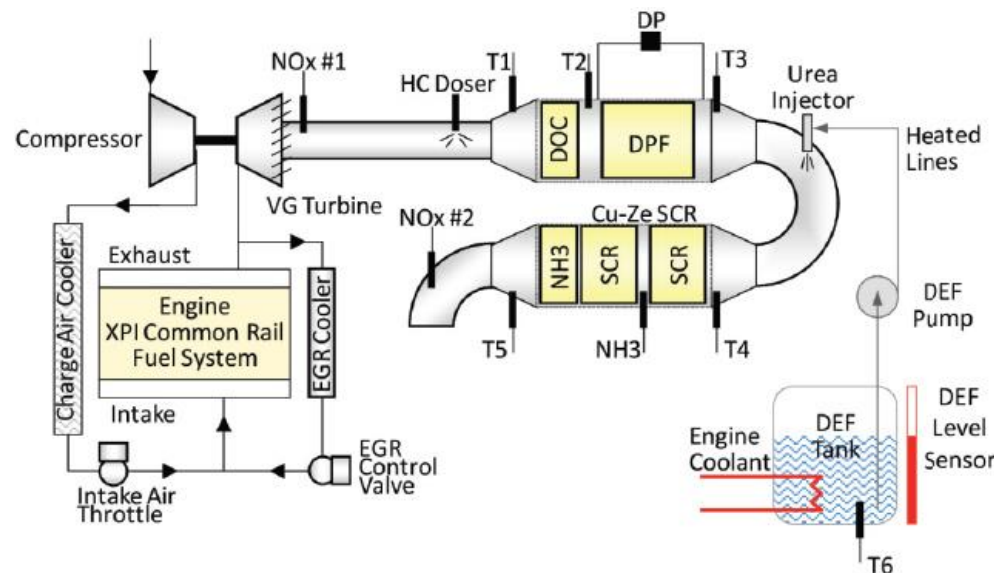
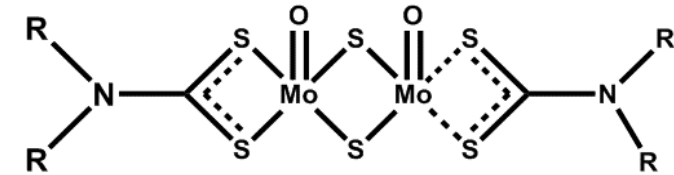
Friction Reducers Types



Ashless

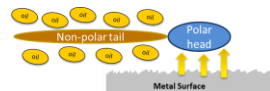


Organometallic

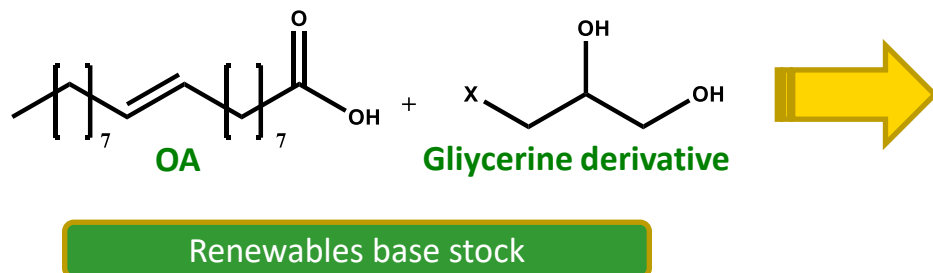


Preferred are ashless organic Friction Reducers, because the organometallic ones can interact negatively with the after treatment devices

New Friction Reducer



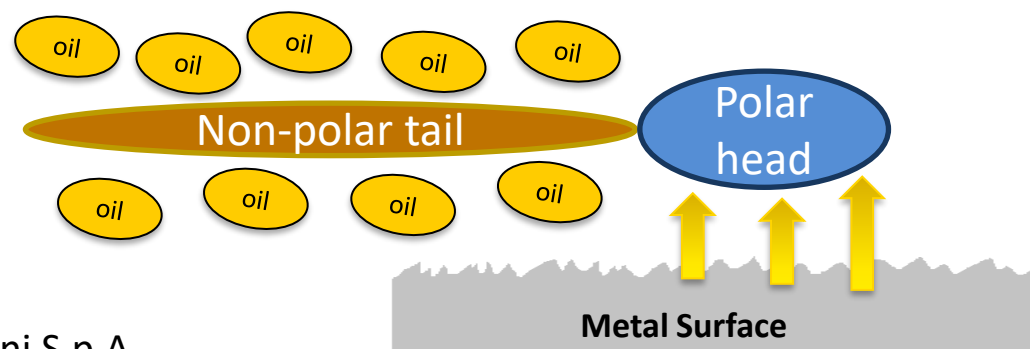
- Eni developed a new bio-based friction reducer additive derived from oleic acid and a glycerine derivative



UNIVERSITÀ DI PISA

Synthesis process with high conversion of reactants and the ratio between the products which guarantees:

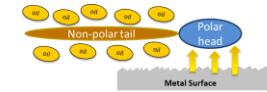
- Solubility in the lubricant***
- Outstanding friction reducing performances***



Patent: WO2022043891A1 - Eni S.p.A.



Tribological tests on new Friction Reducer: MTM test

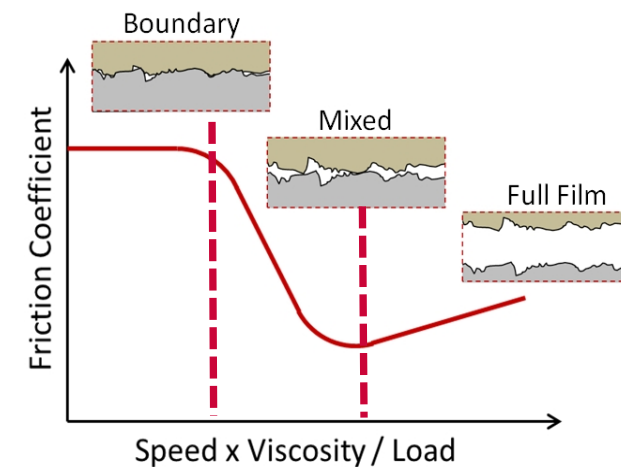


Tribology is the science that studies friction and wear of surfaces sliding in opposite directions

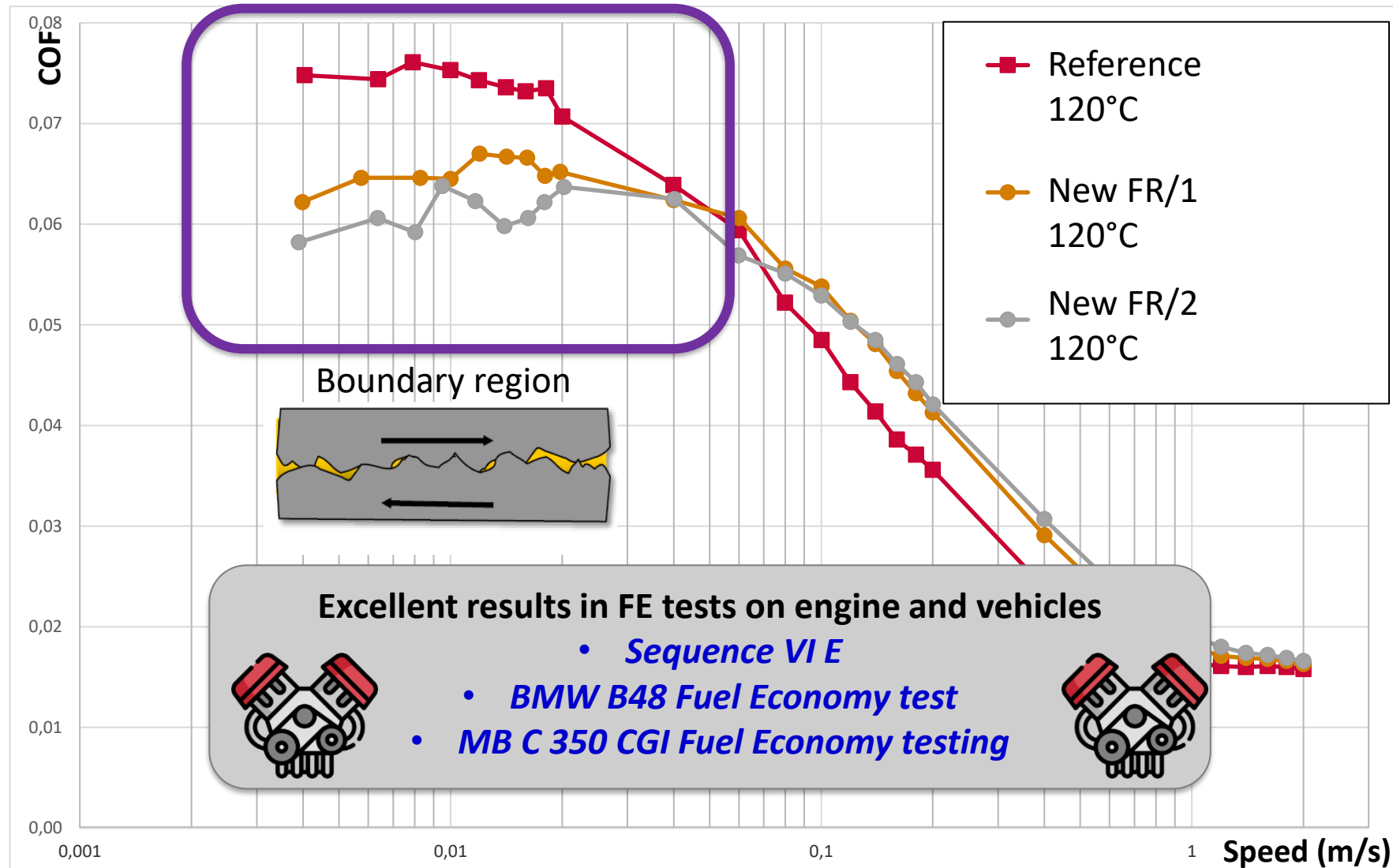
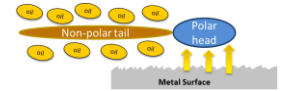


The Mini-Traction Machine (MTM) is an instrument for measuring the friction coefficient of lubricated surface contacts

Typically a ball is in contact with a disc and the friction coefficient profile is recorded in the form of a Stribeck curve



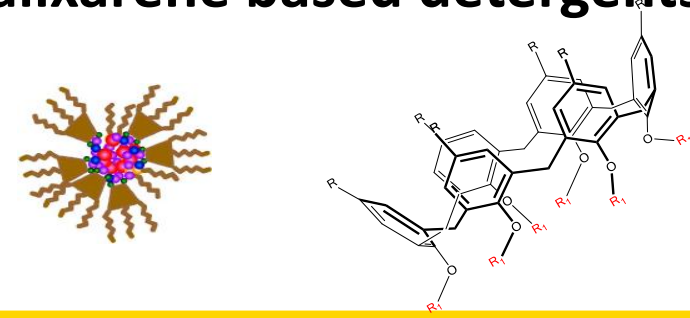
MTM tests and engine tests on 0W-20 lubricants containing the new FRs



Can we do without ZDDP?... What's new in Eni

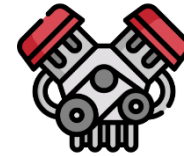
1

Calixarene based detergents



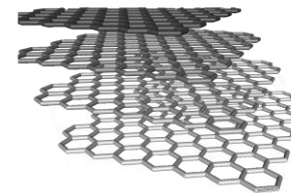
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Organic bio-based friction reducers

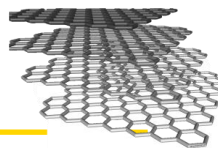


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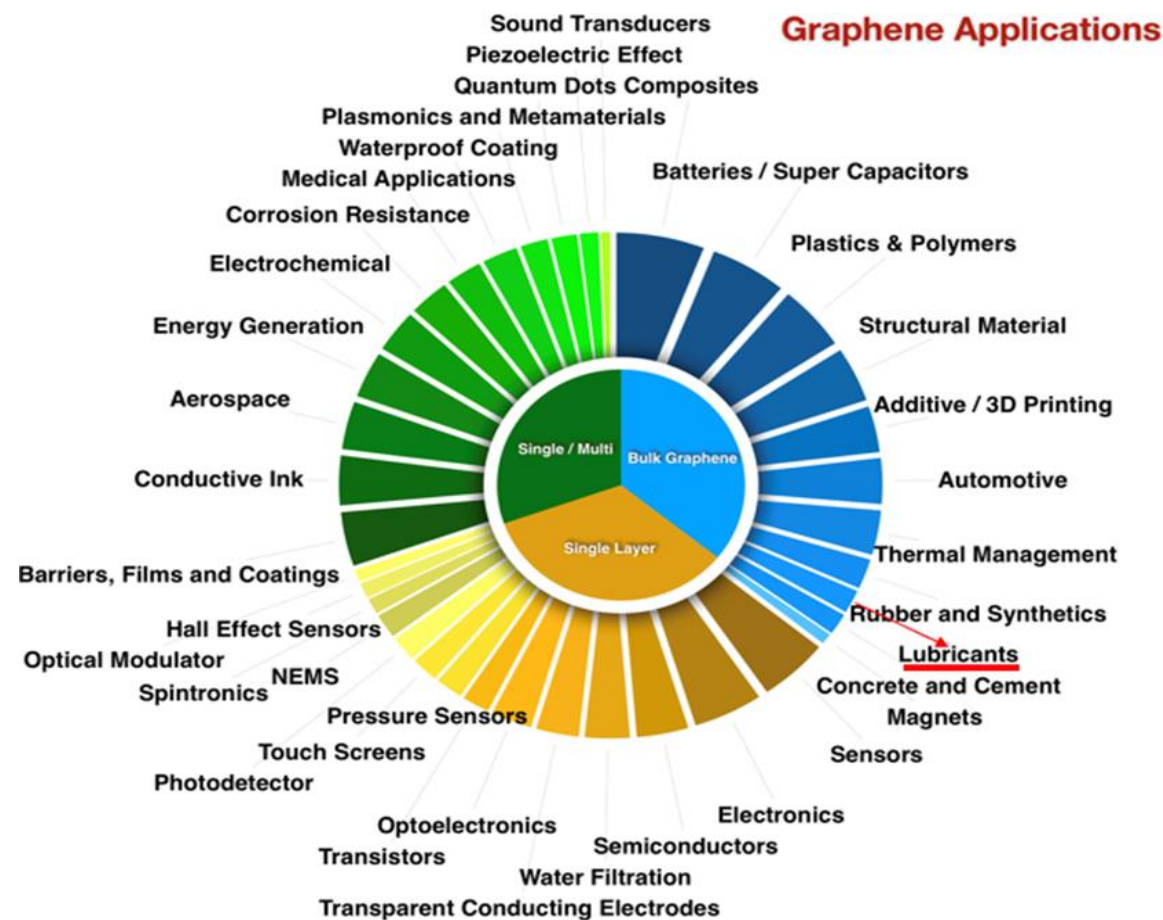
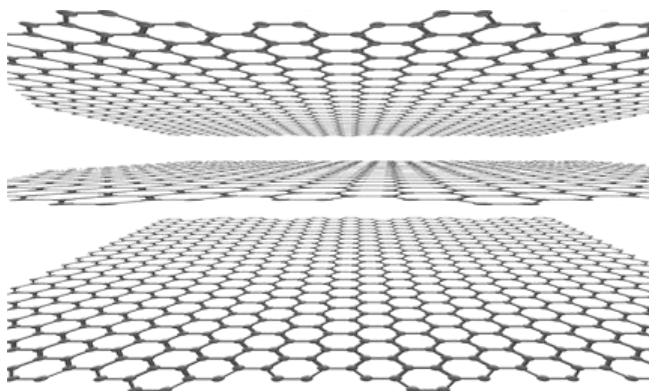
Nano-Additives for friction and wear reduction



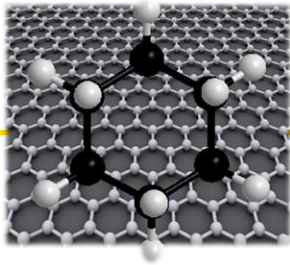
Nano Additives based on Graphene



- Graphene is a single layer of carbon atoms arranged in a honeycomb lattice isolated in 2004 by scotch-tape method from graphite
- Considering the high costs of mono-layer graphene, most applications use FLG (Few Layers Graphene) composed by a number of layers between 2 and 10



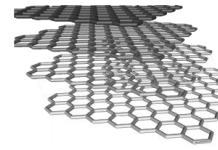
Application of Graphene as Nano Additive for Lubricants



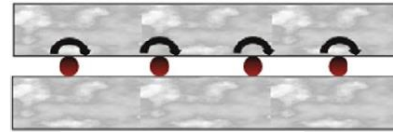
- Outstanding anti-friction and anti-wear properties
- High chemical stability
- High surface area
- High thermal conductivity
- 100% metal free
- High electrical conductivity

Eni R&D is focused on the study of nano additives based on Graphene and in particular on FLG as friction reducers and antiwear for applications in fuel economy lubricants

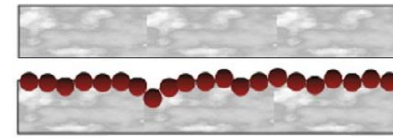
Mechanism of graphene action on surfaces



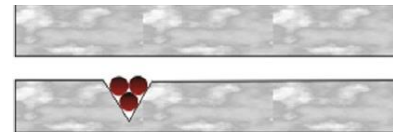
- *Rolling effect*



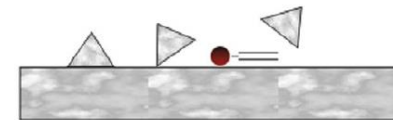
- *Protective film*



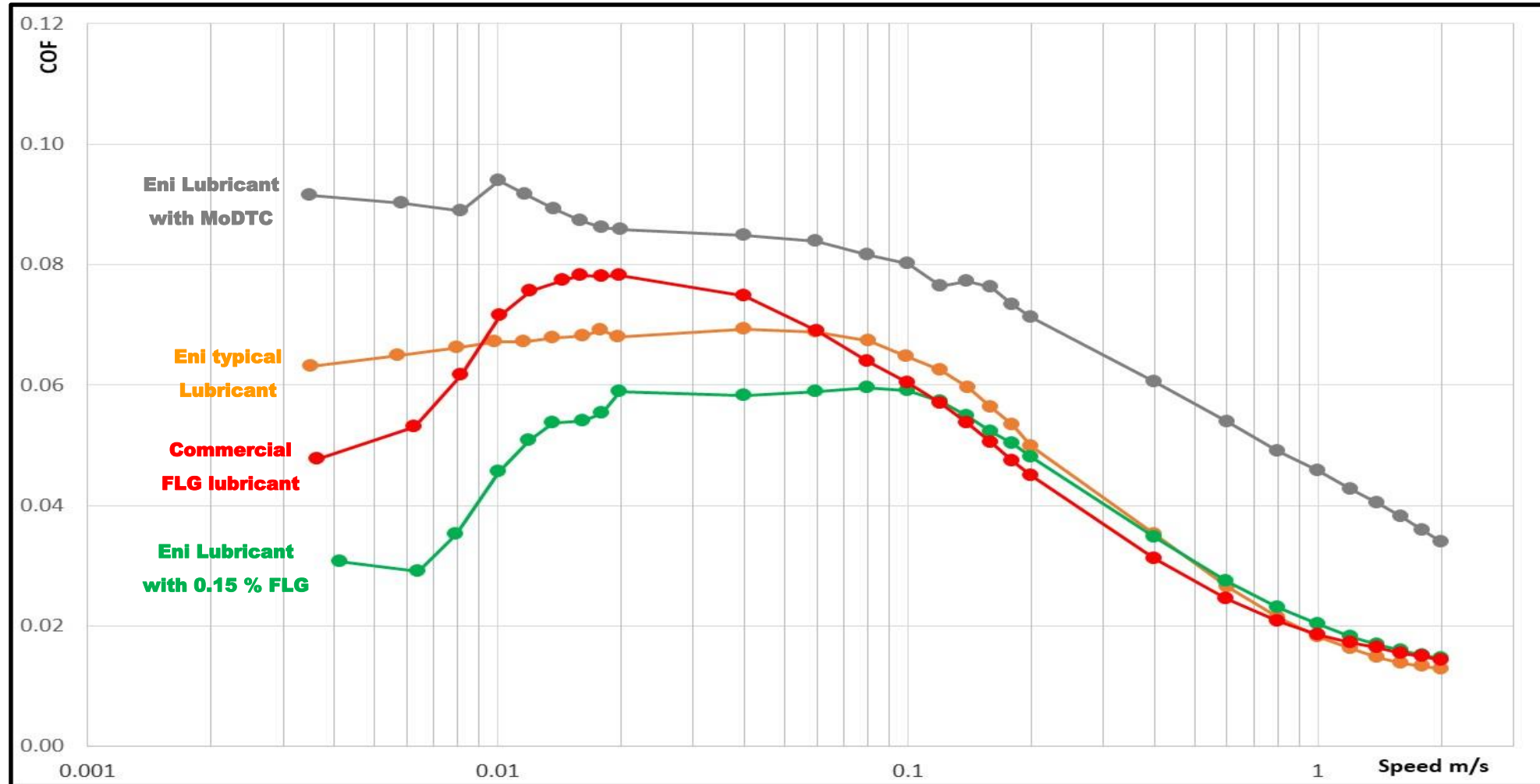
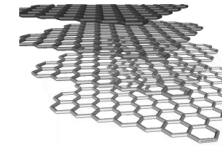
- *Mending effect*



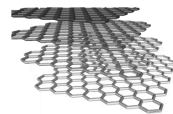
- *Polishing effect*



MTM tests on 0W-20 lubricants containing FLG



Nano – additives for lubricants



PRO



01

100% metal-free



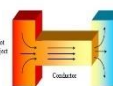
02

Suitable for replacement of organometallic additives



03

Outstanding friction reducing and antiwear properties



04

Improve the heat removal (high thermal conductivity)



CONS



01

Dark Color

Can we manufacture a lubricant without ZDDP?

Currently not!

But...

- ☐ New components can be used to minimise P, S, organo-metals in the lubricants
- ☐ Current possibility to minimize the usage of ZDDP
- ☐ Challenge to find one component with ALL characteristic in one goal as ZDDP
- ☐ Challenge to optimize the new formulation in order to improve the compatibility of different components

