# עמידות החומרים בכלי אחסון ושינוע של דלקי מאובנים ודלקים עתידיים


## אליק גרויסמן

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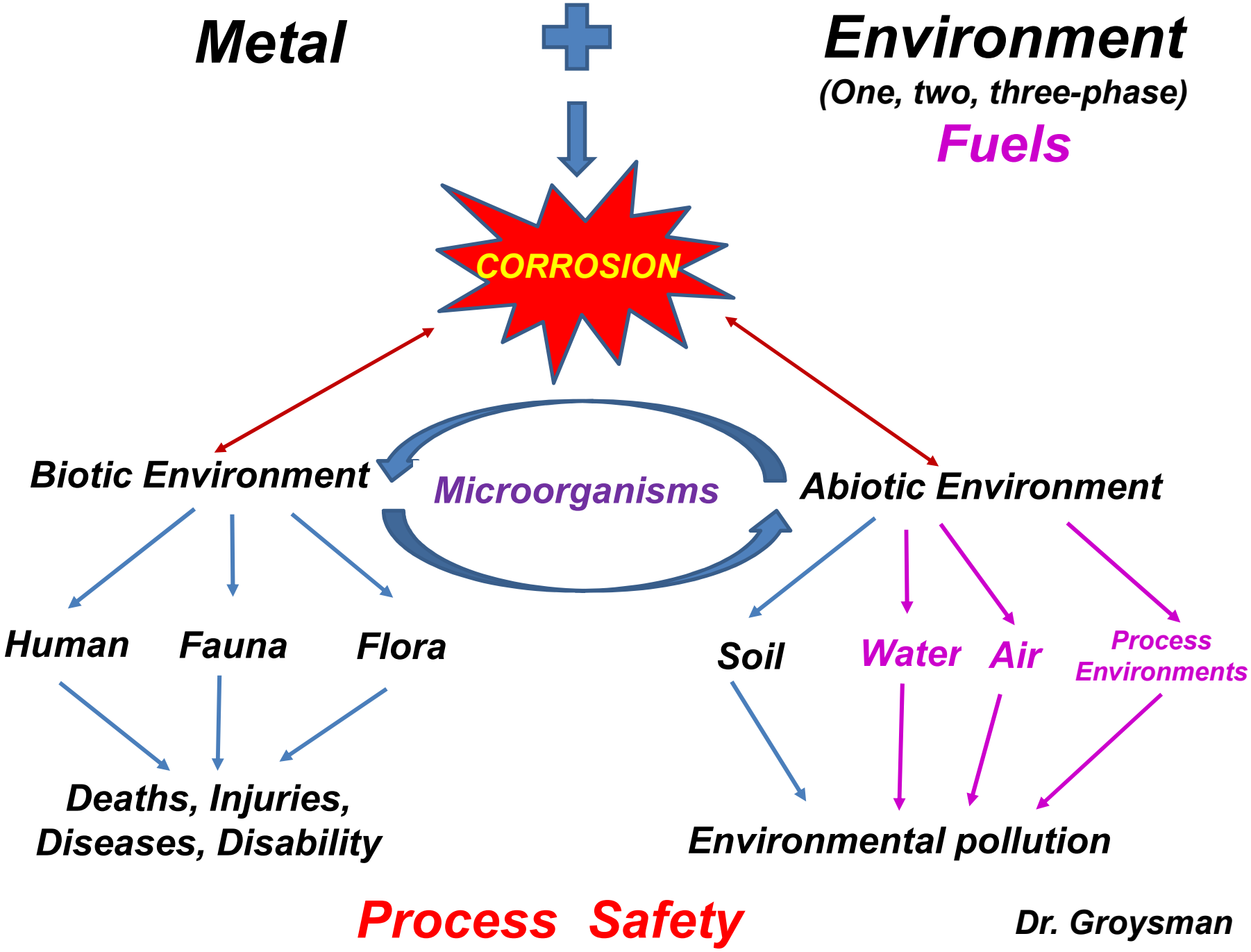
אגודת מהנדסי כימיה וכימאים, לשכת מהנדסים

טכניון, פקולטה להנדסה כימית, תכנית "אנרגיה"

חדשנות בדלקים והשפעתם על הסביבה

19 דצמבר 2018


Metal
Environment
(One, two, three-phase)
Fuels
CORROSION
Biotic Environment
Microorganisms
Abiotic Environment
Human
Fauna
Flora
Soil
Water
Air
Process Environments
Deaths, Injuries,
Diseases, Disability
Environmental pollution
Process Safety
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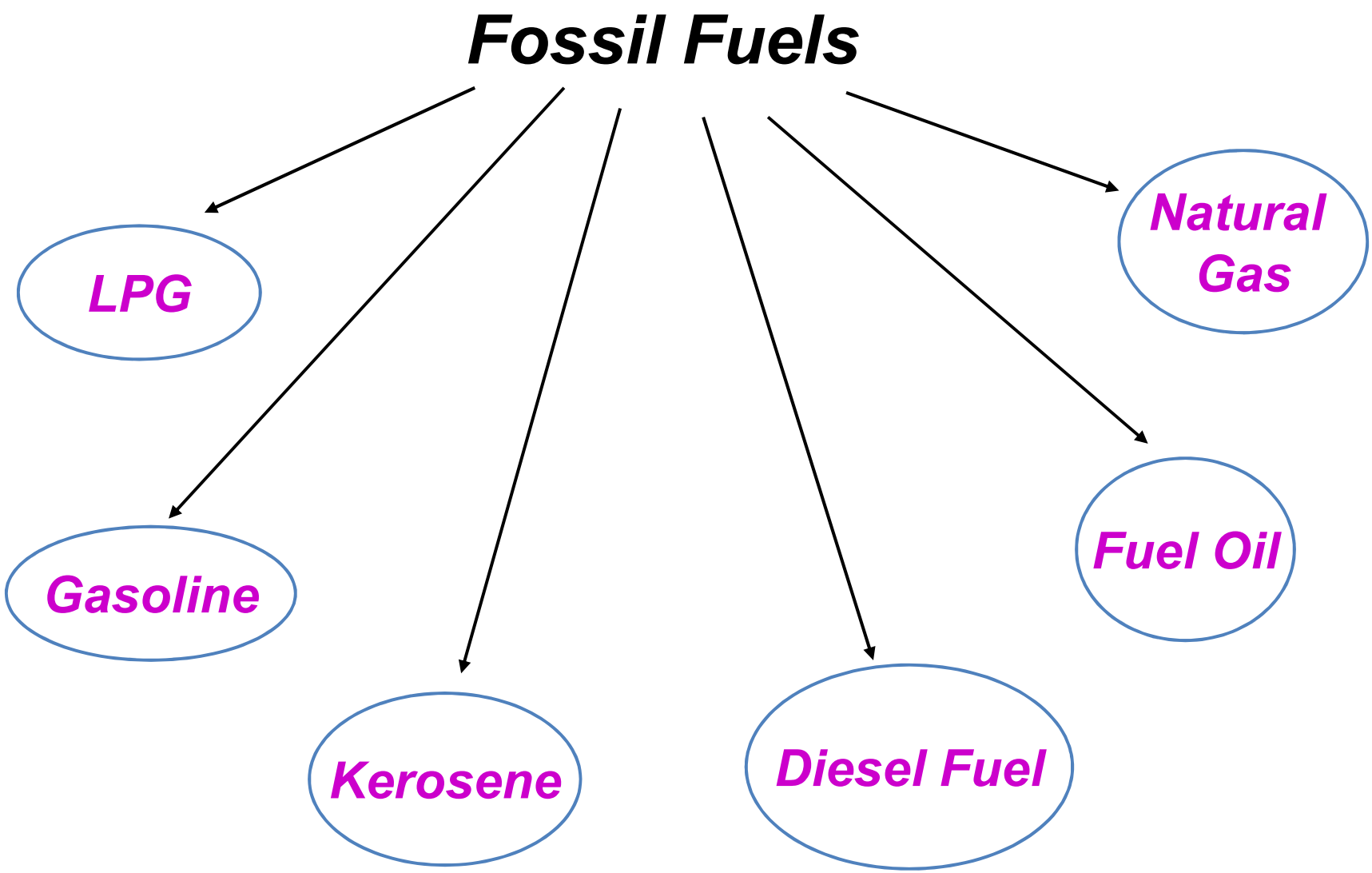


C O R R O S I V I T Y ?

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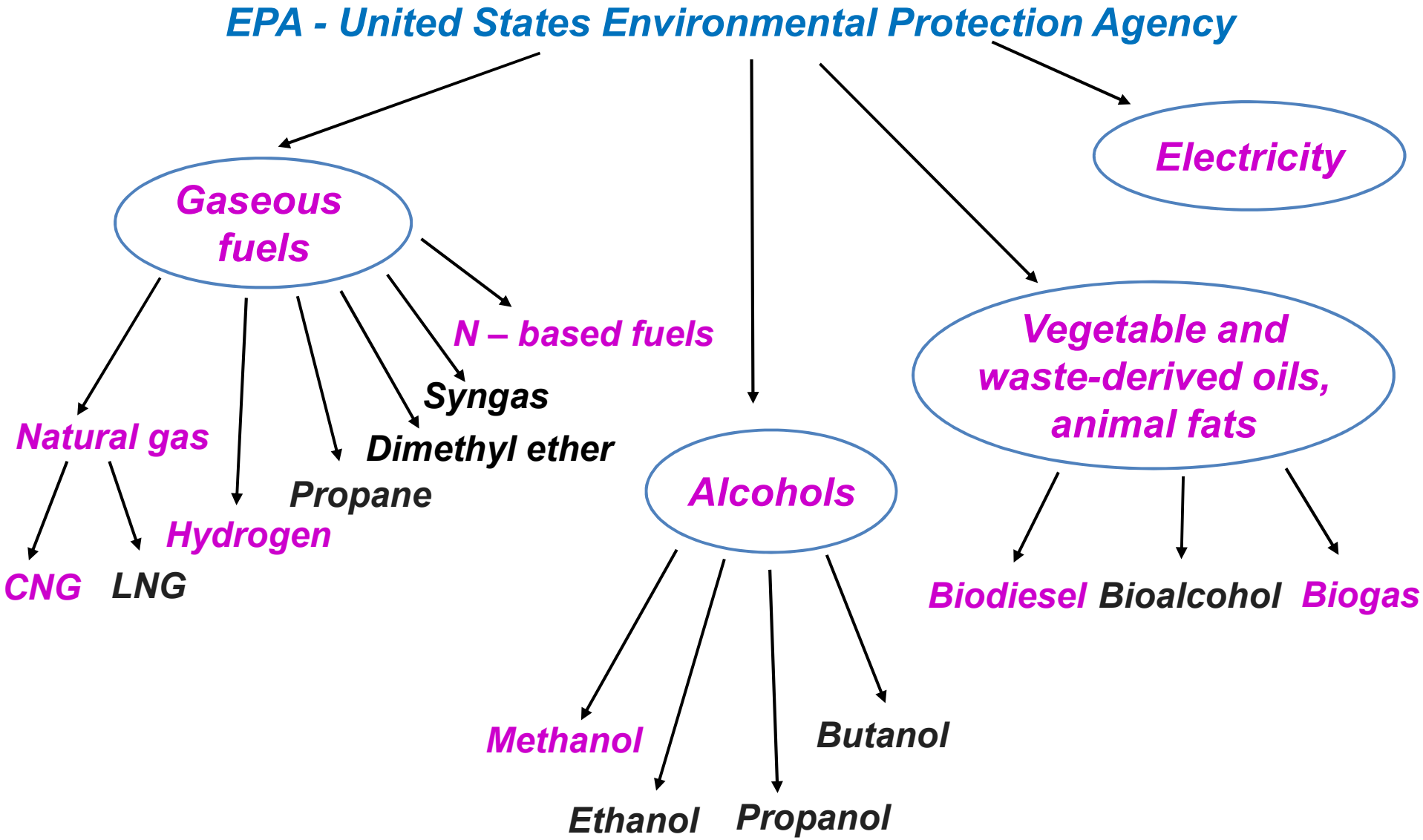
# Alternative Fuels




C O R R O S I V I T Y ?

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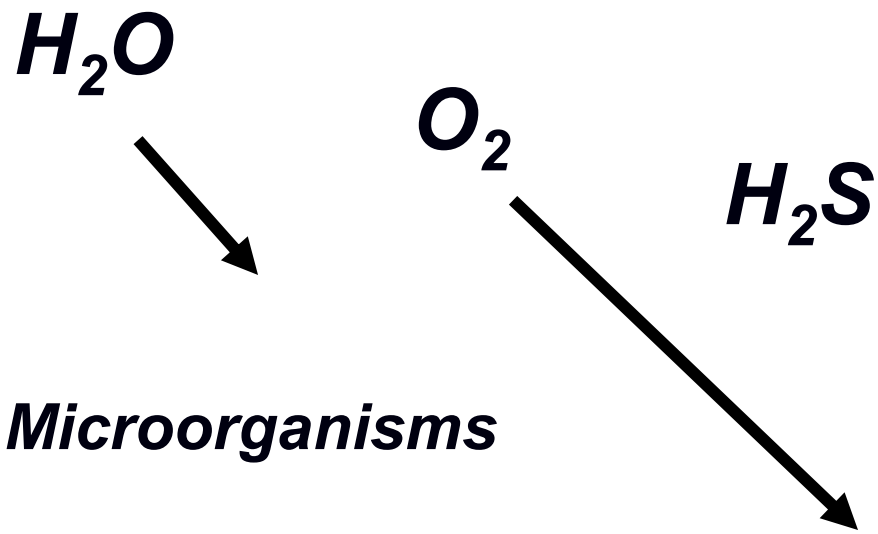
# *Corrosiveness of Fossil Fuels*

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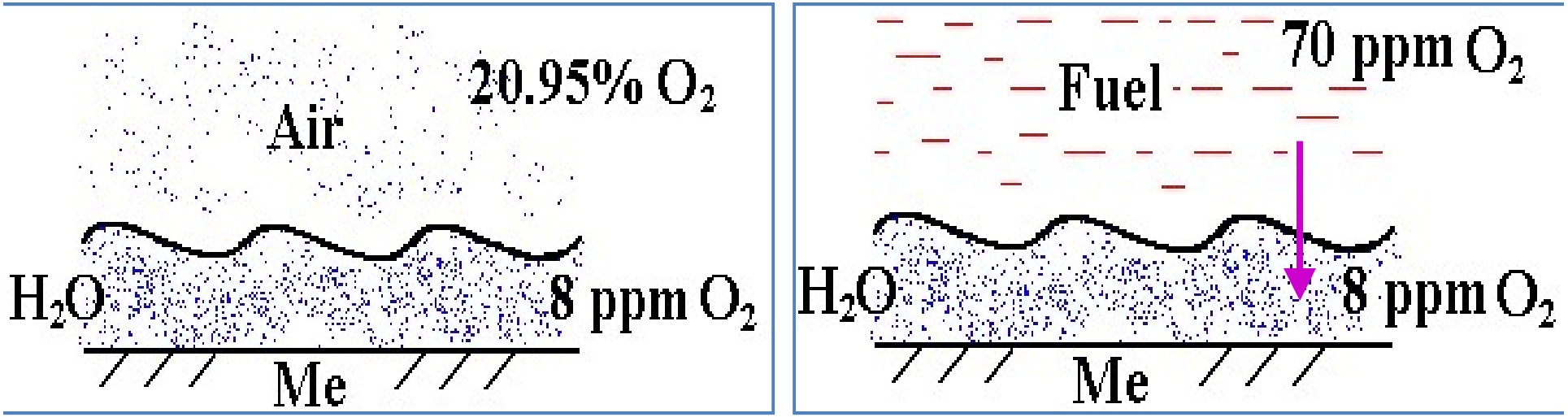
# *Corrosion Mechanism*

***in atmosphere*** ***in fuel***




***Uniqueness:***
***Fuel is a reservoir of oxygen***

***Common: cycle "drying – wetting"***

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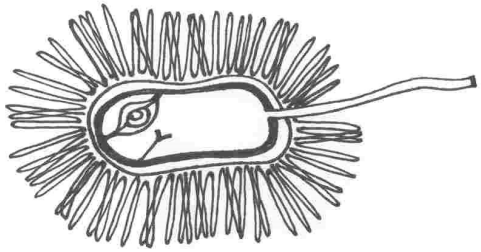
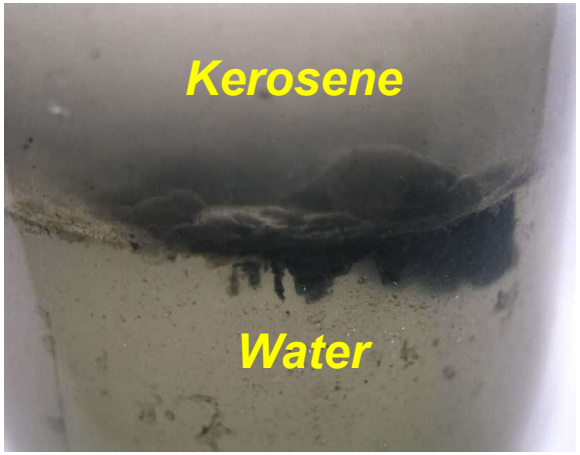
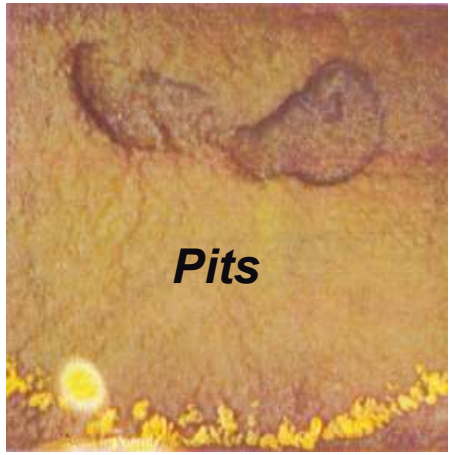
# *Microbial Contamination of Fuels*



***18 years***


***Bottoms of the crude oil AST***

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# *LPG Underground Tank*

***20 years***

***Liquid phase***



***Vapor phase***

***Solution:*** ***- Epoxy coat (550-600 $\mu$m)***

***- Vapor Corrosion Inhibitors***

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# Systems Containing Fossil Fuels

Production → Transportation → Storage and Distribution →

→ Dispensing Stations → Vehicles

**Carbon Steel**

**Stainless Steels**

**API 620, API 650**

**Aluminum** **Zinc** **Cast iron**

**Copper** **Brass** **Bronze**

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# Polymeric Materials in Gasoline

***Swelling of the elastomers***

| Media | | Polymer | | |
|---|---|---|---|---|
| | | NBR | Viton | Teflon |
| Gasoline | Neat (100%) | R | NR | R |
| | + 15 % vol. MTBE | R | NR | R |
| | + 35 % vol. BTX | NR | R | R |
| BTX (100 %) | | NR | R | R |
| MTBE (100 %) | | R | NR | R |

***Certain polymers, and fiberglass are compatible with fossil fuels***

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# Corrosion in Biofuels

## Quality specification for Methanol

| Substance or property | Permitted Value, ppm max |
|---|---|
| Ethanol | 50 |
| Acetone | 30 |
| Water | 1,000 |
| Chlorides (as $Cl^-$) | 0.5 |
| Sulphur | 0.5 |
| Acidity (as acetic acid) | 30 |
| Total iron | 0.1 |

International Methanol Producers & Consumers Association, Brussels, Belgium, 04 October, 2012, 15 p.

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## *Corrosion rates ($\mu$m/year) of metals/alloys in Methanol-Gasoline blends, 40°C, 2000 – 8000 hours*

| *Metal/alloy* | *M85* | *M15 (Aqueous phase)* |
|---|---|---|
| *SS 304* | *0* | *0* |
| *Tin* | *0.2* | *0.5* |
| *Carbon steel* | *1.8* | *7.6* |
| *Brass* | *6.4* | *6.7* |
| *Zinc* | *13.9* | *2.1* |
| *Cadmium* | *22.9* | *35.7* |
| *Aluminum alloys* | *24 - 63* | |
| *Terne plate* | *86.9* | *12.9* |
| ***Magnesium*** | ***146380.0*** | |

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## *Corrosion rates of CS and SS in pure Ethanol and its mixtures with water, 20°C, 3000 hours*

| *Water content in Ethanol, mass %* | *Corrosion Rate, μm/year* | |
|---|---|---|
| | *Carbon steel* | *Stainless steel* |
| *0* | *2.2* | *0* |
| *10* | *3.1* | *0.005* |
| *30* | *-* | *0.146* |
| *50* | *-* | *0.257* |

## *Ethanol-Gasoline Alternative Fuel*

*Alloys Al6061 and Al319, SS 304, and grey cast iron.*
*Anodizing and plasma electrolytic oxidation (PEO) -*
*oxide coatings on the Al6061 and Al319 alloys.*
*All these materials are compatible with the alternative fuels.*

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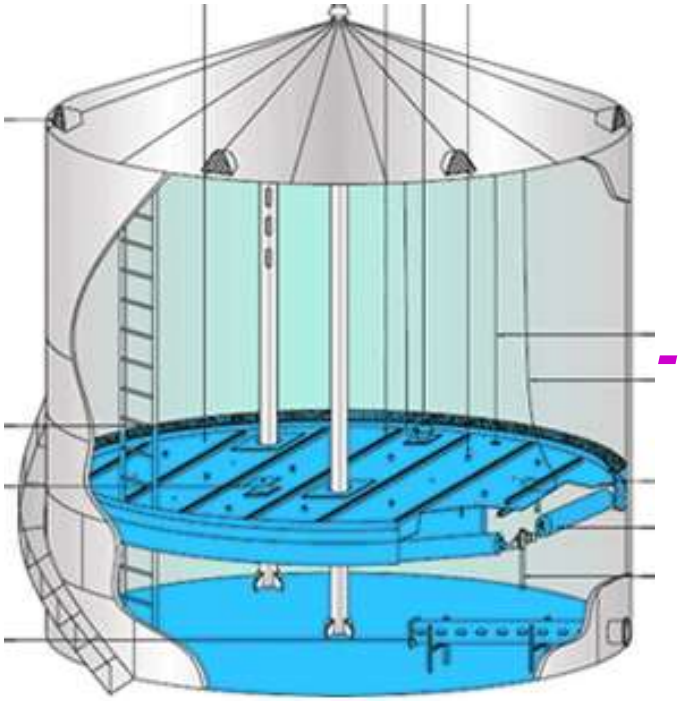
***Alcohols* loosen rust and dirt from the surface**

***Methanol, ethanol and their blends with gasoline are stored in fixed roof tank with an internal floating roof***



***- Nitrogen blanketing***

***- Dehumidification of air***

***Corrosion inhibitors for prevention corrosion***

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# Corrosion in Biodiesel (Ethyl or Methyl ester)

***Biodiesel can be produced from any source having oil, either of animal or vegetable source: soybean, castor, palm, cottonseed, sunflower, macauba, rapeseed, jatropha, animal fat (tallow), and residual oils.***

## Quality specification for Biodiesel (B100) ASTM D6751, EN 14214

| Substance or property | Permitted Value, max |
|---|---|
| Methanol | 0.2 vol% |
| Water and Sediment | 0.05 vol% |
| Sulphur | 15 (S15) |
| | 500 (S500) |
| Acid Number | 0.5 mg KOH/g |
| Copper Strip Corrosion | No. 3 |

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# ***Biodiesel – Diesel - Ethanol (BDE) fuel blends***

***CS, Cu and Al were studied by static immersion at 20$^{o}$C and 60$^{o}$C.***

***CR in the order: Al < CS < Cu***

***The degradation of fuel properties and CR of metals in BDE fuel blends are lower than B100, whereas higher than petro-diesel (B0).***

***Maximum of 20 vol% biodiesel and 10 vol % ethanol can be used in diesel engine for better engine performance and emissions.***

***The presence of water, organic acids, aldehydes, peroxides, ketones, and esters in oxygenated fuel causes corrosion in fuel system materials; in addition, degrades the properties of fuel.***

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*Feedstock with higher concentrations of unsaturated HC – oxidation.*

*The rate of corrosion is influenced by:*

- *temperature,*
- *water content,*
- *microbial growth,*
- *type of feedstock used for synthesis of biodiesel.*

*Biodiesel - more dissolved water than diesel fuel*

*Water in biodiesel - proliferation of microorganisms and corrosion*

***Corrosion Rates of CS in biodiesel:***

***0.001 - 0.09 mm/year***

*B0, B50, B100 (27 – 80°C):* **< *0.0015 mm/year*** *(Malaysia)*

*To check the corrosivity of new biodiesel each time (from new source) !*

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## *Materials compatible in contact with Biodiesel*

| Type of Material | Name |
|---|---|
| Metal/Alloy | Aluminum |
| | Carbon Steel |
| | Stainless Steel |
| Polymers | Viton |
| | Fluorosilicone |
| | Fluorocarbons |
| | Polypropylene |
| | Polyethylene |
| | Nylon |

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# *Used Cooking Oils as Feedstocks for Biodiesel Production*

***Waste cooking oil - more corrosive:***

- ***Fatty acids***
- ***Water***
- ***Oxidized products***
- ***Unsaturated molecules***
- ***Metallic – organic compounds***

***The free fatty acid (FFA) content and water content (moisture content) are the main parameters to be analyzed.***

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## *Corrosion Rates of CS, Cu, Al in Used Cooking Oil, B100, Diesel Fuel*

| Diesel Name | TAN, mg KOH/g | Corrosion Rate, mm/year | | |
|---|---|---|---|---|
| | | CS | Cu | Al |
| Used Cooking Oil | 0.97 | 0.05 | 0.0125 | ≈ 0 |
| B100 | 0.36 | | 0.0075 | ≈ 0 |
| Diesel Fuel | 0.29 | | 0.025 | 0.0088 |

*[ Malaisia, Zamir Yusoff, 2015-2016]*

*SS - immune to pitting corrosion.*
*Al, Cu, Cu alloys, CS – prone to pitting corrosion.*

*[Singh et al., 2012]*

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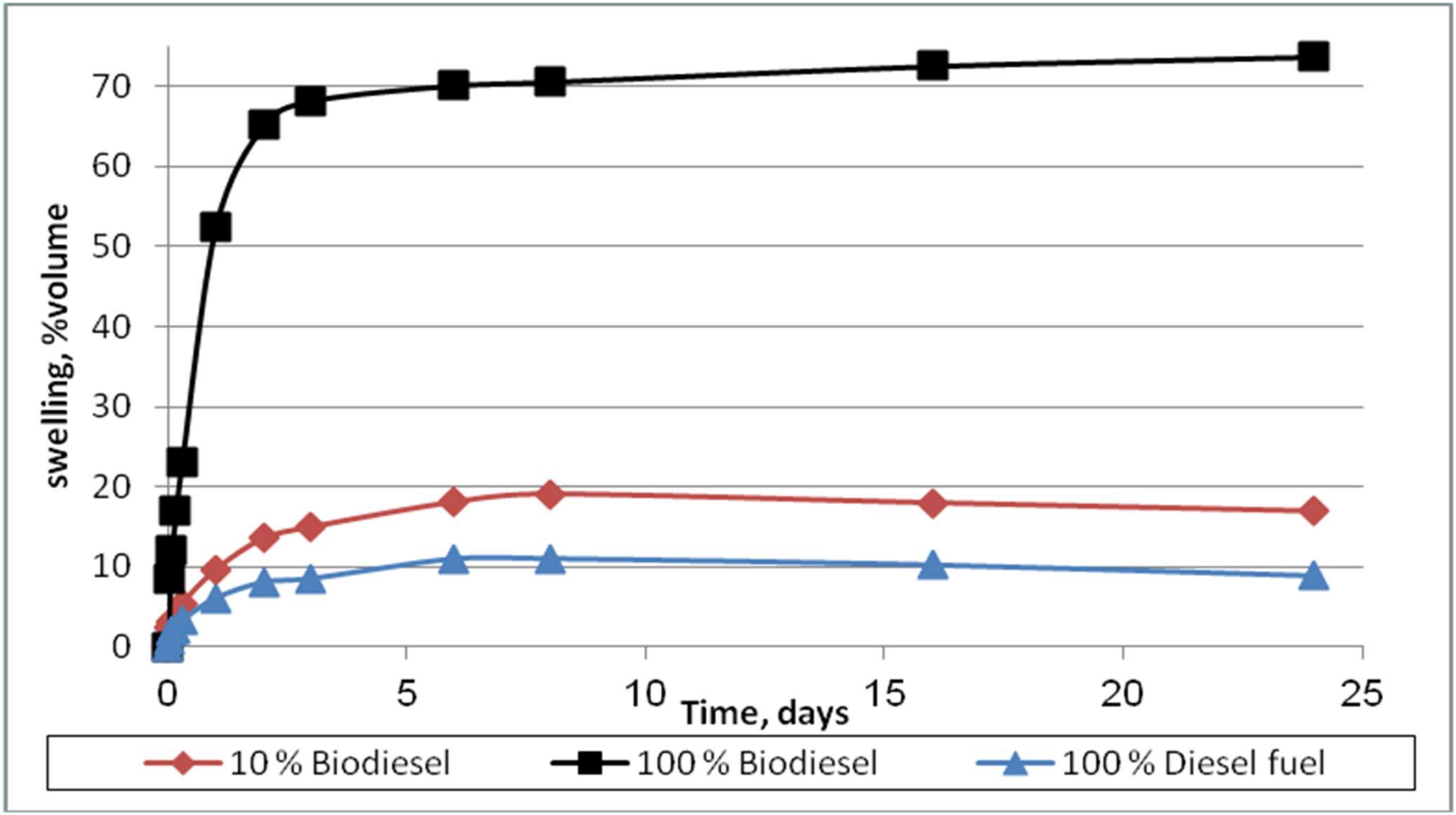
## *Kinetic curves of polymers' swelling (% vol.)*
## *Neoprene 50 in three types of fuel, 22°C*




***The polar nature of elastomers causes the dissolution in the biodiesel***

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# Corrosiveness of Natural Gas

| | | |
|---|---|---|
| Methane | $CH_4$ | 70-99% |
| Ethane | $C_2H_6$ | 0 - 20% |
| Propane | $C_3H_8$ | |
| Butane | $C_4H_{10}$ | |
| **Carbon dioxide** | **$CO_2$** | **0-8%** |
| **Oxygen** | **$O_2$** | **0-0.2%** |
| Nitrogen | $N_2$ | 0-5% |
| **Hydrogen sulfide** | **$H_2S$** | **0-5%** |
| Noble gases | He, Ne, Ar, Xe | trace |

**$H_2O$** **Hg**

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# *Material Choice in NG Systems*

***Carbon steel occupies more than 90% of all the materials in NG systems. (API 5D, 5CT, 5L. Corrosion allowance: 1.5-6 mm. Corr. control methods.)***

***Materials compatible with corrosive media – Corrosion Resistant Alloys.***

***Stainless steels; Alloys Ni, Co, Cu, Ti, Al; Polymers; Composite materials.***

***Carbon steels → stainless steel martensitic 13Cr → stainless steels austenitic → duplex stainless steels → austenitic nickel alloys.***

***We may select alloy: CR < 0.05 mm/year***

***Iron-nickel (9%) alloys - for cryogenic tanks for storage of LNG at –162°C.***

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# *Corrosion in Nitrogen-Based Fuels*

***A low carbon Nitrogen-based alternative fuel, consisting of an aqueous (25 %) urea (15 %) and ammonium nitrate (60%) solution.***

***pH = 5.8–6.0***

***It is nonexplosive, nontoxic, safe to handle, and can undergo continuous, stable and environmentally friendly combustion with the formation of effluent gases 73.0% $H_2O$, 21.6% $N_2$, and 5.4% $CO_2$ (moles).***

***By-products: CO, $NO_x$, and short-lived radicals.***

***It is crucial to find suitable construction materials of the reactors and process pipelines for this fuel.***

***[M. Starostin, G. S. Grader et al., Technion, 2014-2018]***

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*The aqueous UAN solution and its combustion products are very corrosive, and their aggressiveness increases considerably at high temperatures 550-750$^{o}$C.*

*Austenitic SS 316L, 310S, 330 were tested under 20 MPa , 745$^{o}$C and 545$^{o}$C for 200 hours.*

*The tested alloys were subject to an aggressive media containing water vapor, nitrogen oxides, carbon oxides, ammonia, and other intermediate species including radicals under a high pressure and high temperature.*

*[M. Starostin, G. E. Shter and G. S. Grader, Technion, 2014-2018]*

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*The heaviest corrosion - SS 316L in the hot reaction zone. No protective Cr-rich oxide films were found in the scales formed on all tested SS.*

*8.0 mg/cm$^2$ was observed after 200 h at 745$^o$C.*

*The corrosion of 310 and 330 SS at the same conditions was significantly lower: 1.3 and 0.9 mg/cm$^2$ respectively.*

*The scales formed on the SS specimens were porous, cracked, and non-uniform.*

*Corrosion inhibition of carbon steel in aqueous solution of ammonium nitrate and urea.*

*[M. Starostin, G. E. Shter and G. S. Grader, Technion, 2014-2018]*

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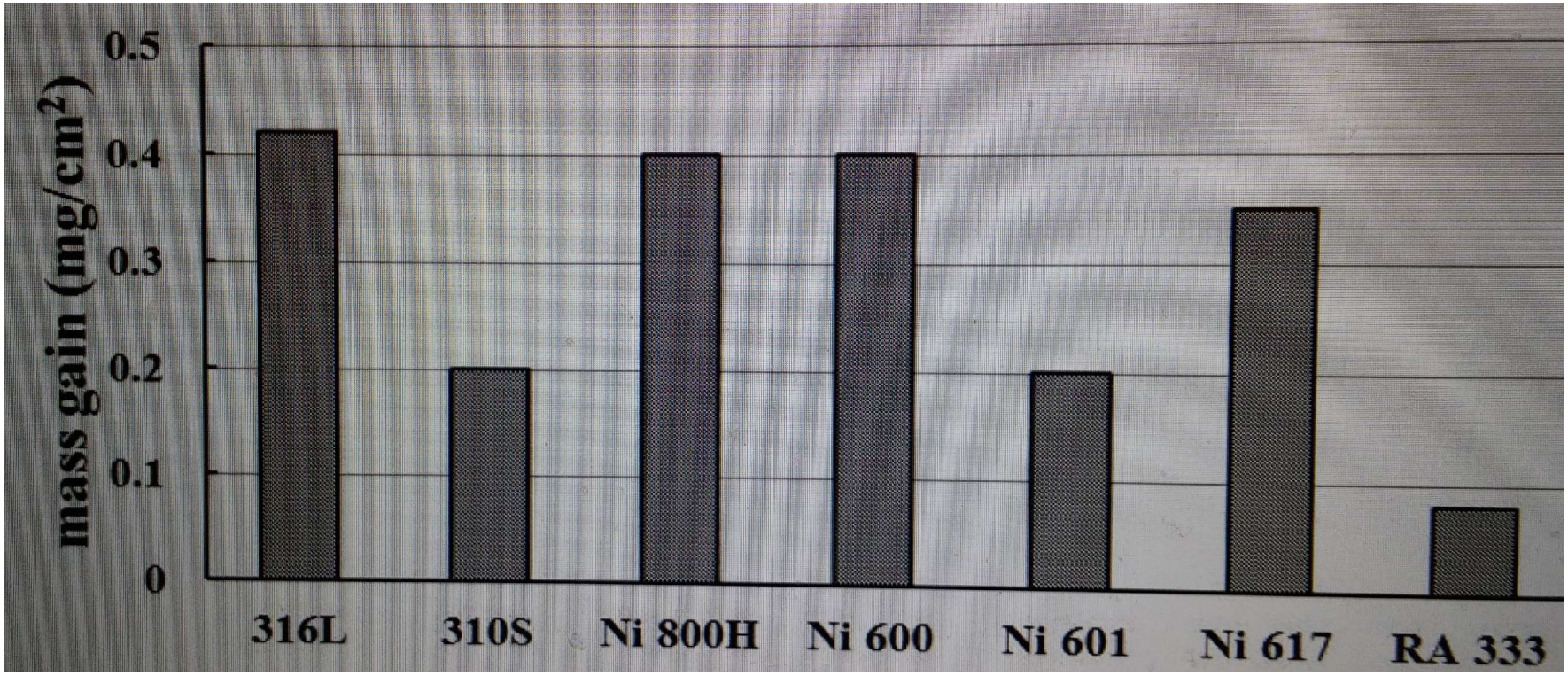
# *Combustion of a Nitrogen-based fuel: aqueous solution of ammonium nitrate and urea*

***Tested materials include SS 316, 310 and nickel alloys: 600, 601, 617, 800H and RA333. The results were received under conditions close to those in practical continuous combustion. The coupons: 520°C and 10 MPa in the effluent gases.***




*[M. Starostin, G. E. Shter and G. S. Grader, Technion, 2014-2018]*

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# *Ammonia energy*

## *Green Ammonia is finally taking off … $CO_2$-free "Gasoline"*

***November 2, 2018***

### *Ammonia-methane or ammonia-hydrogen mixtures*


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*For Ammonia production: air, water and catalysts.*

*A $CO_2$ - Free fuel for combustion engines already exists and is cheaper and safer than petroleum products.*

*TED lesson http://ed.ted.com/on/zahZVhIR*

*Ammonia-gasoline dual fuel, and pure ammonia engines*

*Ammonia is corrosive to Cu, Zn, Ni, and their alloys*



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*Belgium, 1943*

*The X-15 aircraft used ammonia as one component fuel of its rocket engine (1950s)*


*Ammonia Run Toyota GT86-R Eco Explorer By Marangoni 2013*

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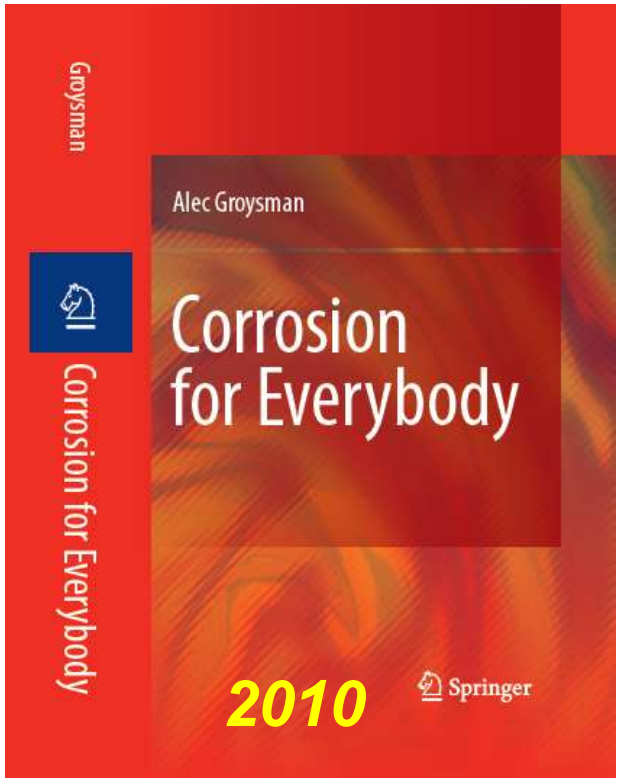
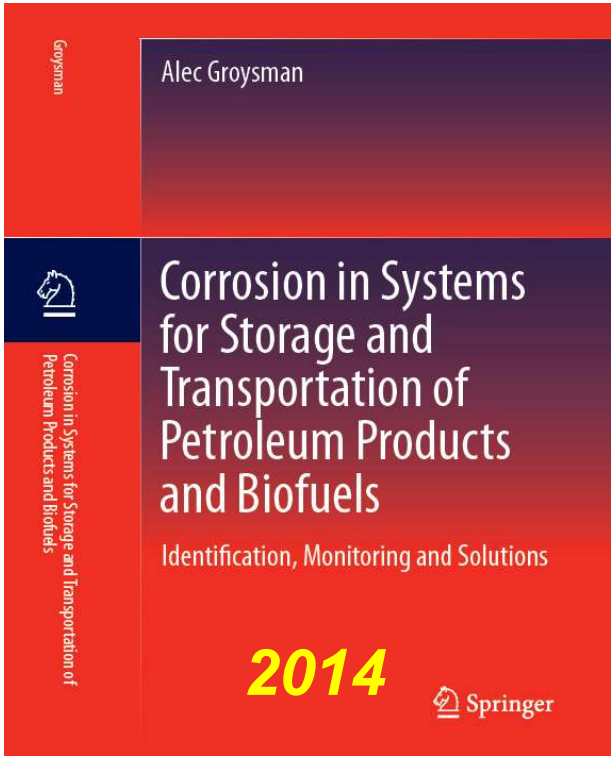
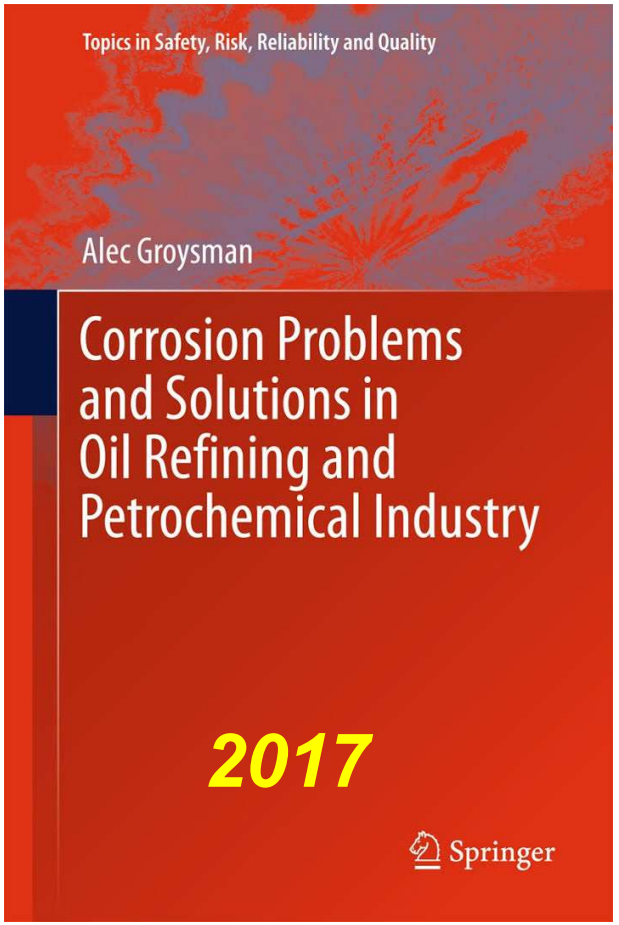
# *PREVENTION IS BETTER & CHEAPER THAN A CURE*

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המכון הישראלי
לאנרגיה ולסביבה

"בית הספר למדעי הנפט והאנרגיה (חל"צ / 186)

# "גז טבעי" – ספר חדש בהוצאת מכון האנרגיה


*Dr. Groysman*