DOTTORATO DI RICERCA IN SISTEMI DI PRODUZIONE & DESIGN INDUSTRIALE

“Modeling of Waste Engine Oil Treatment by means of Inorganic Membranes”

Doctorate School (ScuDo)

Department of Management and Production Engineering (DIGEP)

PhD Candidate of XXV Cycle

In Production Systems: Khurshid Shaymardanov

Supervisor: Prof. Fulvia Chiampo

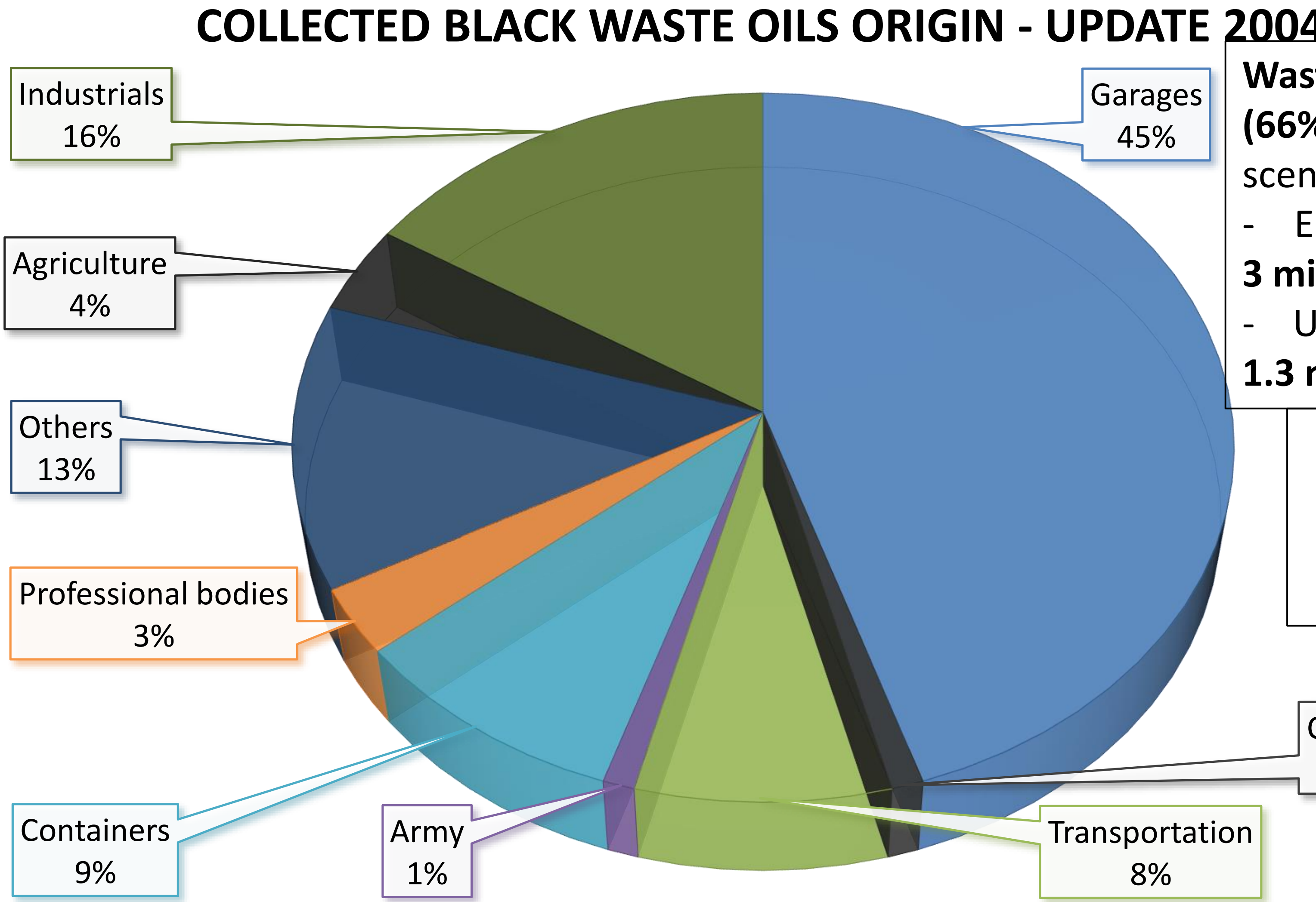
Coordinator: Prof. Luca Settineri

SCUDO DOTTORATO DI RICERCA

POLITECNICO DI TORINO

Contents

1. State of the art:



Waste engine oil (66%) generation scenario:

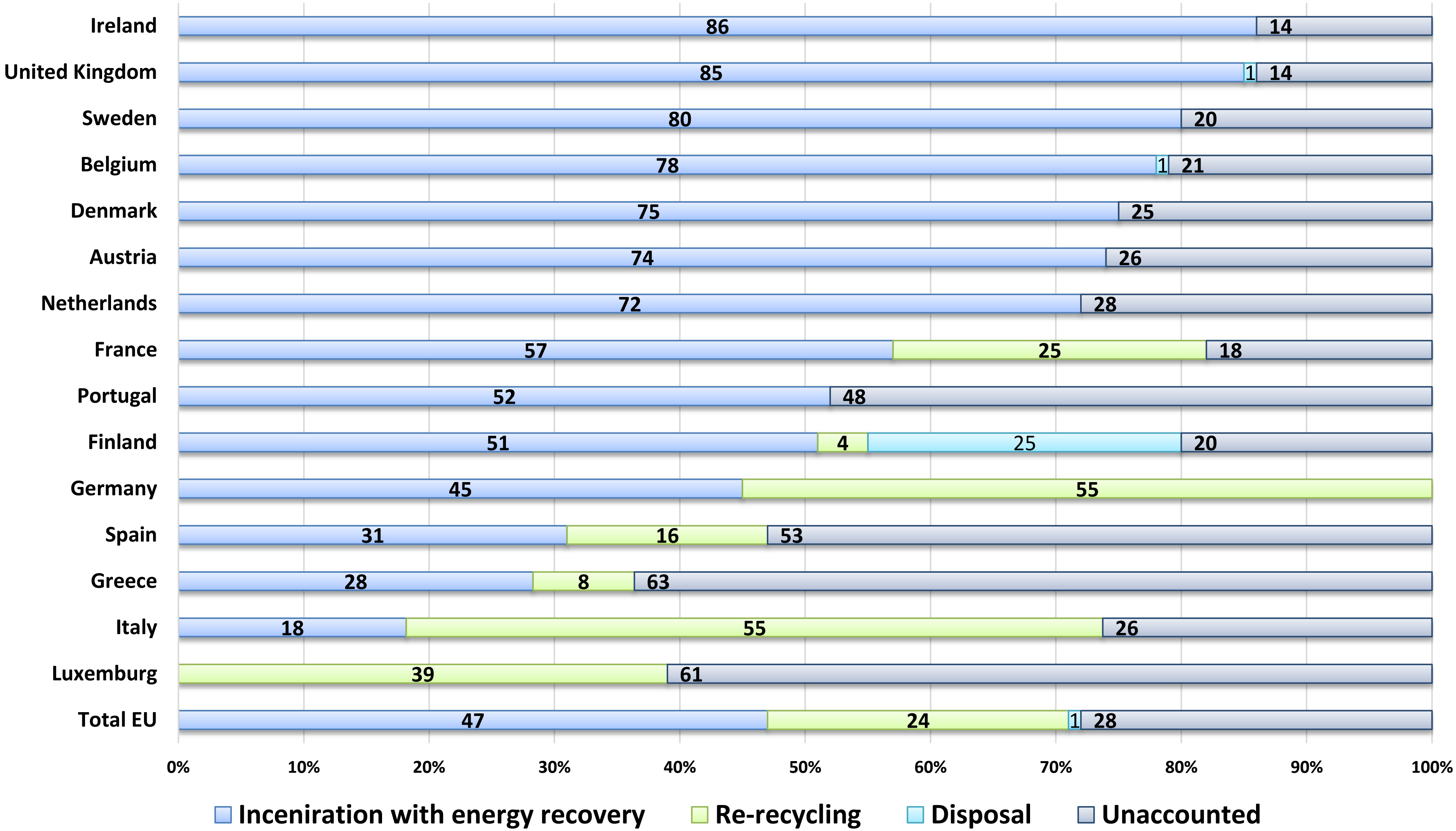
- EU in 2006': **3 million tons**;
- USA annually: **1.3 million gallons**.

Sources:

1. [21]
2. [22]

[Audibert, 2006]

1. State of the art: Waste oil generation, EUROPE

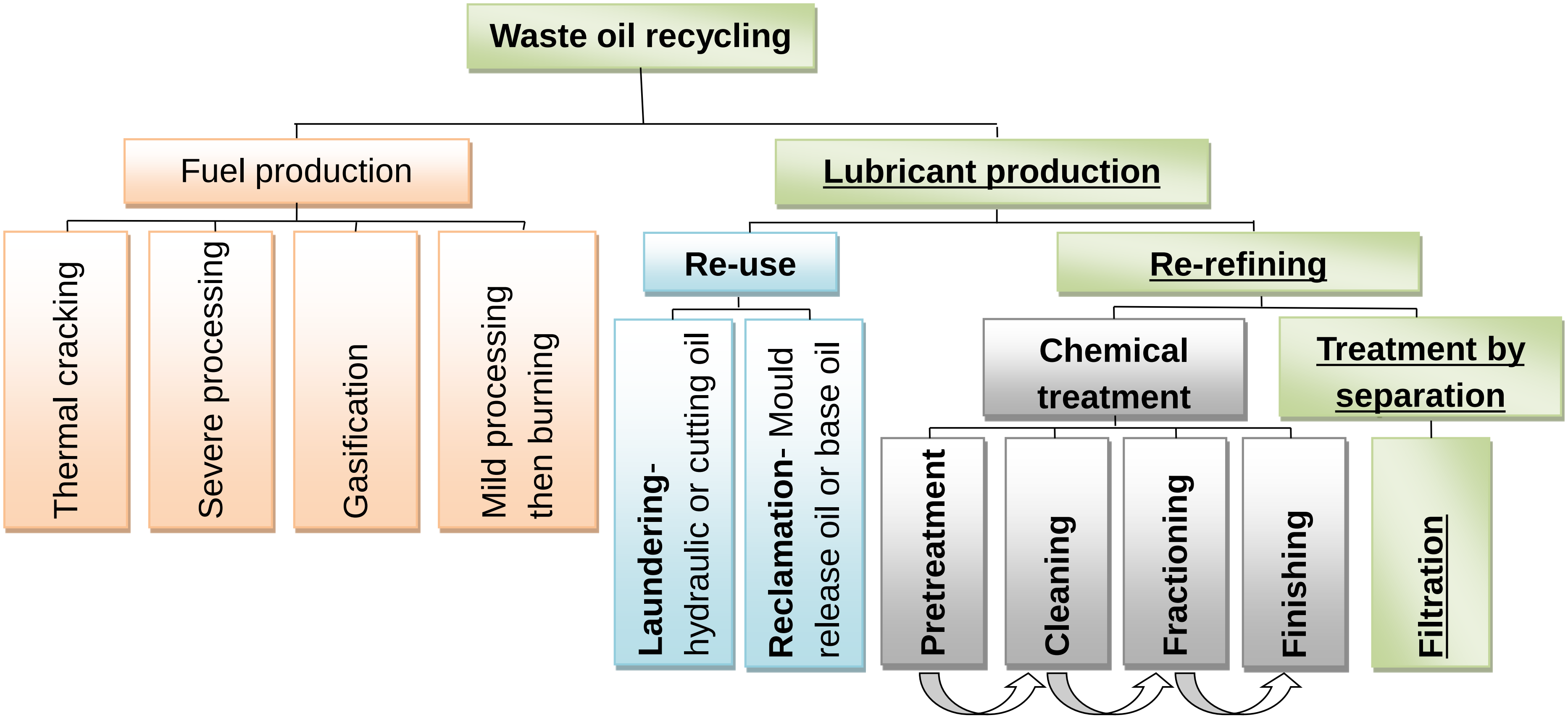


[European Commission IPPC Bureau, 2006]

SCUDO DOTTORATO DI RICERCA

POLITECNICO DI TORINO

1. State of the art: Classification of recycling



[European Commission IPPC Bureau, 2006]

1. State of the art: MF, UF, NF

Organic contaminants	Probable source	Approximate concentration range[a]
	Aromatic hydrocarbons	
Polynuclear (PNA):		
Benzol(a)pyrene	Petroleum base stock	360 - 62 000
Benzol(a)anthracene	Petroleum base stock	870 – 30 000
Pyrene	Petroleum base stock	1670 – 33 000
Monoaromatic Alkylbenzenes	Petroleum base stock	900 000
Diaromatic Naphthalenes	Petroleum base stock	440 000
	Chlorinated hydrocarbons	
Trichloroethanes	Chemical reactions during use of contaminated oil	18 – 1800
Trichloroethylenes	Chemical reactions during use of contaminated oil	18 – 2600
Perchloroethylenes	Chemical reactions during use of contaminated oil	3 - 1300
	Metals	
Barium	Additive package	60 – 690
Zinc	Additive package	630 – 2500
Aluminum	Engine or metal wear	4 – 40
Chromium	Engine or metal wear	5 – 24
Lead	Leaded gasoline	3700 – 14 000

[a] - All values in µg/l, except metals in mg/kg

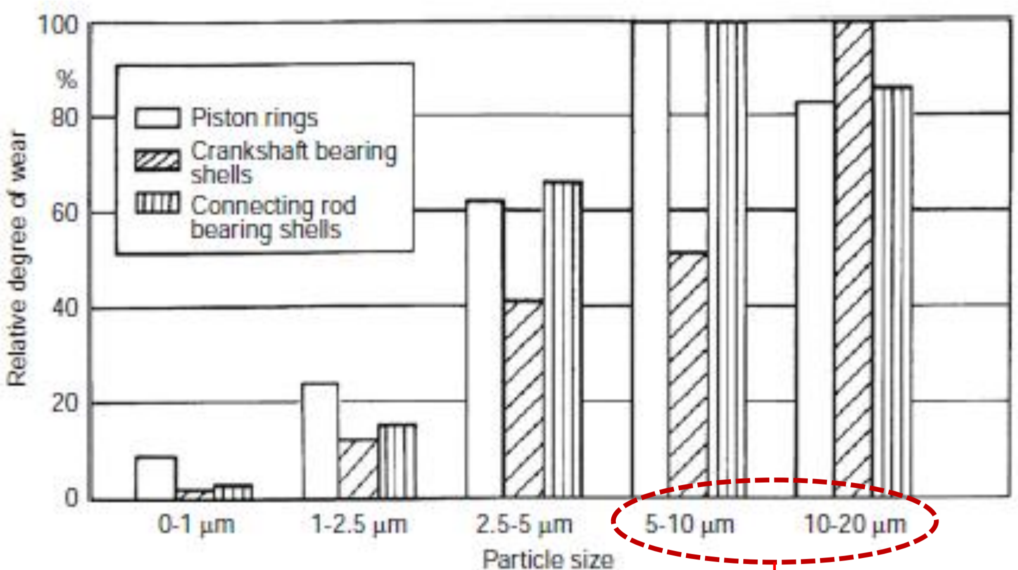
NF

MF

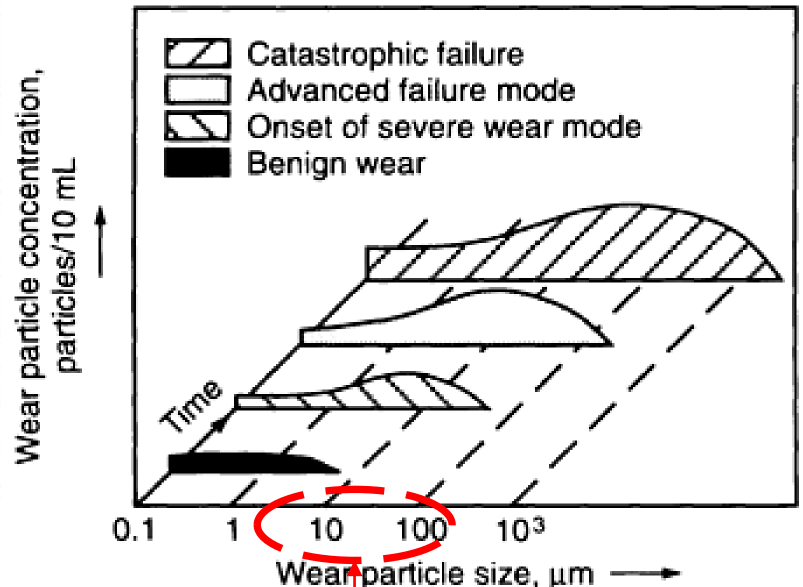
[El-Fadel et al, 2001]

1. State of the art: Wear rate

[Mollenhauer et al, 2010]



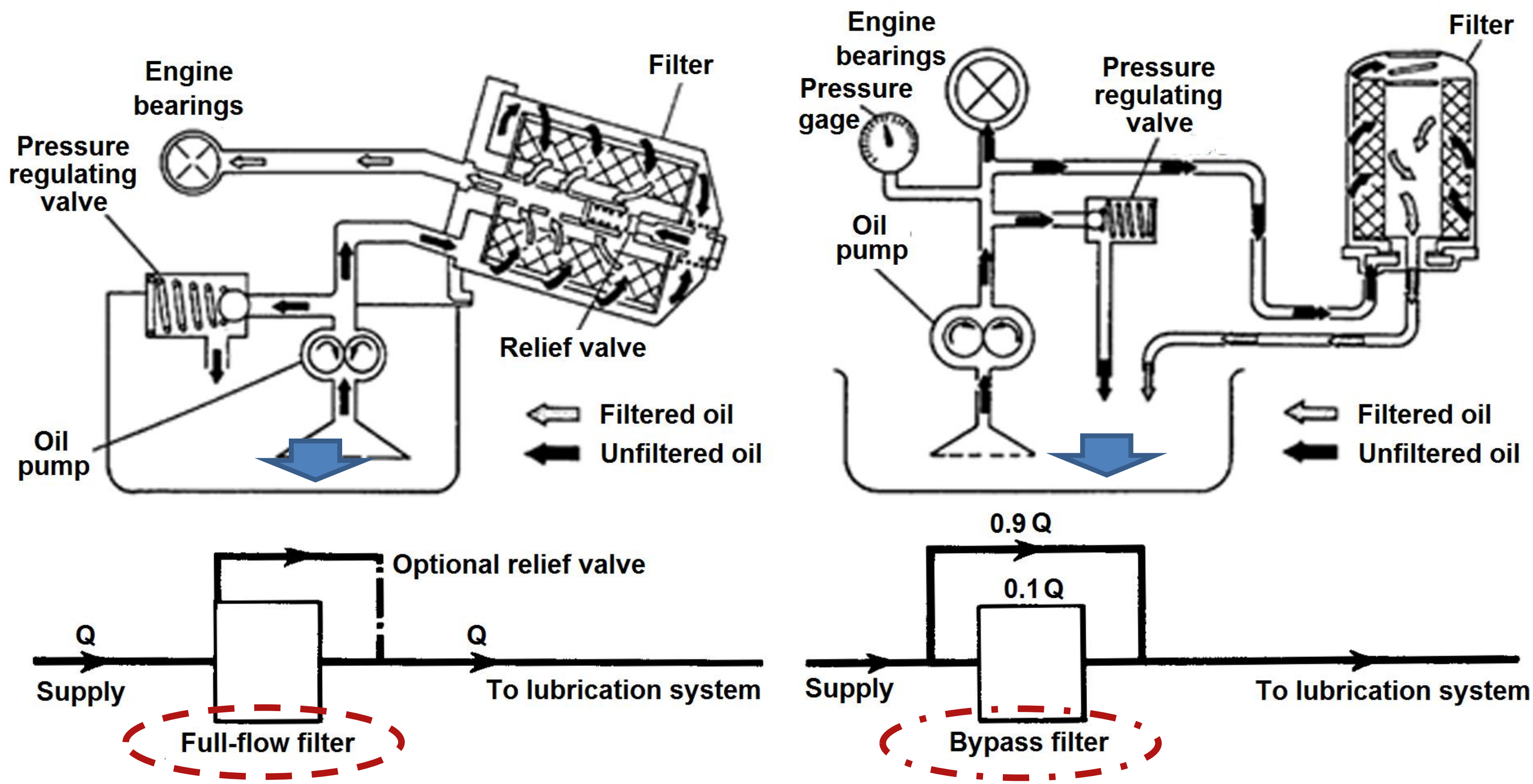
[ASM Int. Comm., 1997]



The images above show how particle size can affect the engine components. Wear in tolerance can be considered if it is below circa 5 µm which is about 50% of piston rings, crankshaft bearing shells and connecting rod bearing shells wear. Hence, to keep this limit, membrane whose maximum permeate is below 5 µm is necessary to be used in such a system.

From the previous slide, one could see that double filtration is recommended to use in the lube system to prevent nano particles to become sticky soot (unwanted by engine components) and support steady state treatment of the system from worn particles

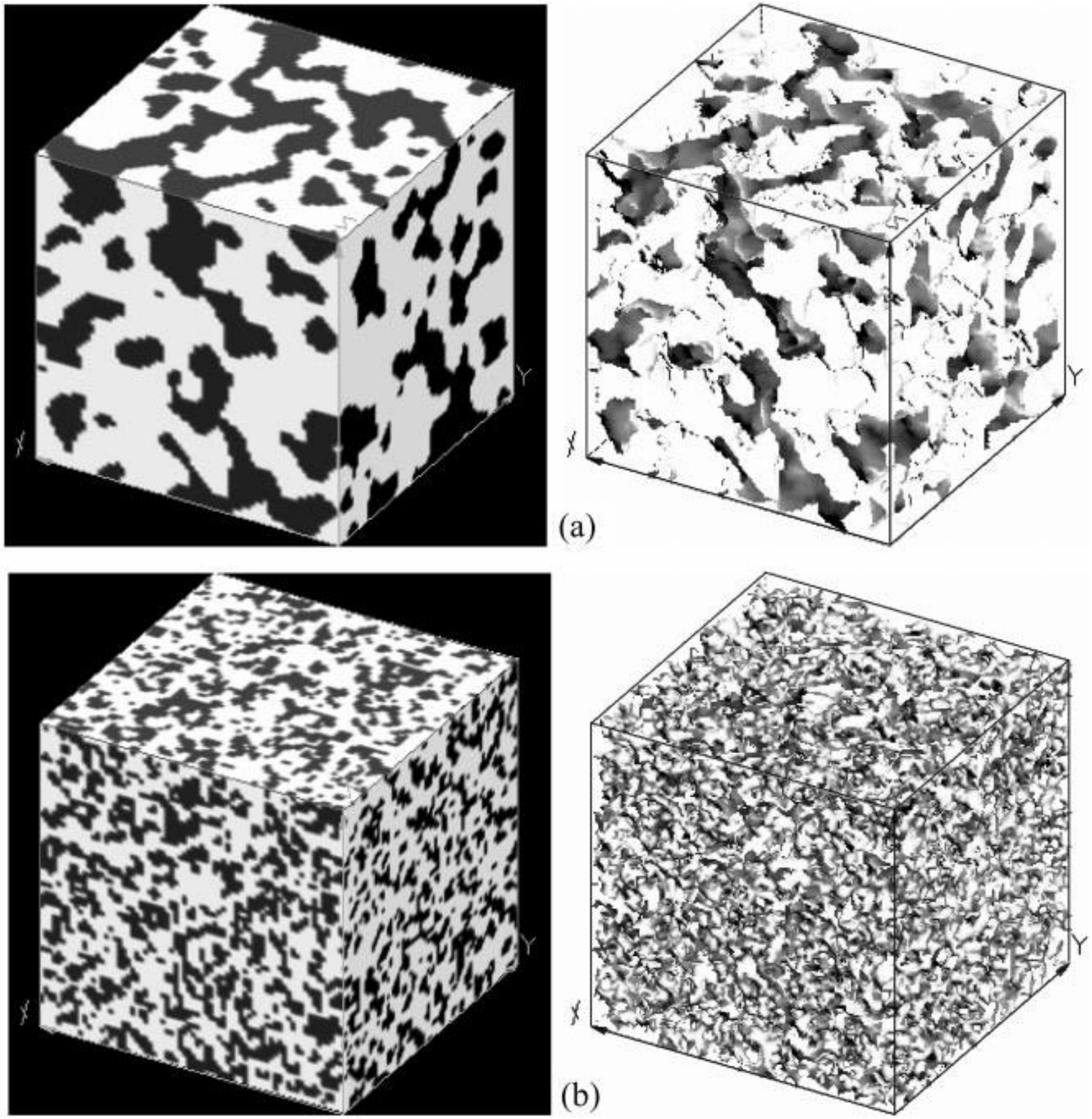
1. State of the art: Possible filtration methods



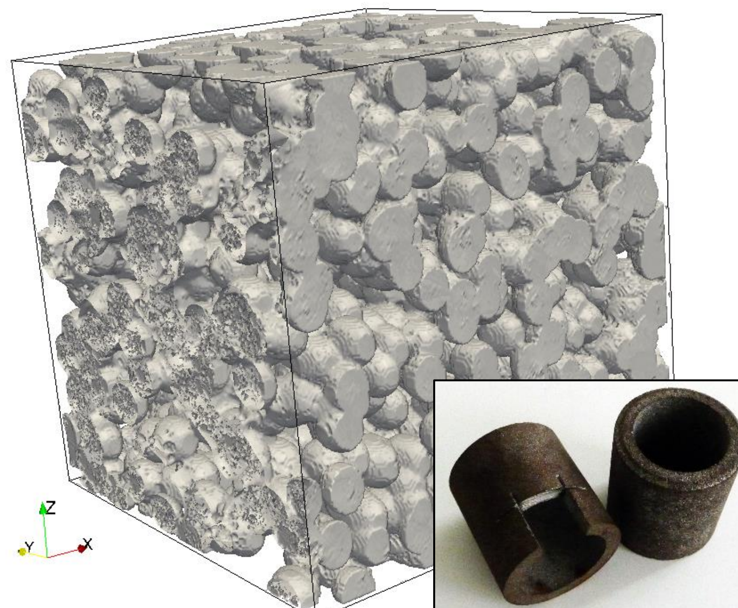
Full flow (a) and **bypass flow** (b) type of **lubricant filters** are already being practiced in lubrication system of an engine.

[US Army Mechanical Course, 2011]

1. State of the art: Membrane



[Singh et al, 2000]:
Comparison of two porous structures having the same porosity, 40% and different pore length
Image a)-top has 0.05 and image b)-bottom 0.5 correlation length values or tortuosity.



2. Aims (scope) of the work

1. Waste engine oil treatment: perform pore scale simulation of the single phase flow through the porous complex medium;
2. Application of the metal-ceramic membranes to treat the waste oil;
3. Application of the membranes in-situ on engine;
4. Development of the reliable methodology to design metal-ceramic based membranes;
5. Recommendations to improve existed membrane parameters;
6. Investigation of optimal parameter of the filters;
7. To fit the specific needs of membrane customers.

3. Theory

- Reynolds number for flow in the porous media:

$$Re^* = \frac{\chi U \rho_f}{\mu(1-\varepsilon)}; \ (1)$$

where, χ – average size of membrane grains, ε – membrane porosity, ρ_f – fluid density, U – velocity, μ – dynamic viscosityof the fluid; [Rhodes,2008]

- Kozeny-Carman equation of permeability for a packed bed, the laminar flow:

To be computed by LBM

$$k = \frac{D^2 \varepsilon^3}{C(1-\varepsilon)^2}; \ (2)$$

where, D – average size of membrane grains, ε – membrane porosity, C – a geometrical shape factor; [Hwang, 2009]

- Computing with LBM's discrete Boltzmann equation by tending local relaxation time τ to 0, Chapman-Enskog solved Boltzmann equation for Navier-Stocks equation according to BGK model for incompressible viscous fluid:

Finite difference method

$$\frac{1}{c_x^2}\frac{\partial P}{\partial t} + \nabla u = 0; \ (3)$$

$$\frac{\partial u}{\partial t} + u\,\nabla u = -\nabla P + \nu \nabla^2 u; \ (4)$$

where P=p/ρ and the kinematic viscosity $\nu = \frac{(2\tau-1)}{6}\frac{\delta_x^2}{\delta_t}$, p- independent pressure, ρ – fluid density, [He, 1997]

Lattice Boltzmann method

- Darcy's equation for flow-rate estimation:

$$Q = \frac{-kA\,(P_b - P_a)}{\mu L}; \ (5)$$

where, k – membrane permeability, Pb-Pa – pressure drop across membrane, μ – dynamic viscosity of fluid, L – membrane thickness

4. Methodology

The sequence of the work flowed according to following scheme:

- Obtaining, gaining any **tubular inorganic membrane**;
- Gaining **several waste engine oil samples** for the study;

1.Sample preparation

- **Analysis of the lubrication system** to know if the flow in the lubrication system is laminar, transient or turbulent;

2.Image Analysis

- Membrane surface **image acquisition** with the **aid of SEM**;
- Membrane **material approval with EDS** results;
- **Image processing** with **ImageJ software**;

3.Modelling - Computational fluid dynamics

- Based on the results of the image processing, **reconstruction of 3D morphology** of the membrane with help of Matlab, C++, ParaVIEW;
- **Simulation of the waste engine oil passing through the reconstructed membrane** pores in order to evaluate the permeability with help of PALABOS software (based on LBM);
- **Based on Darcy's (flow rate)** and Kozeny-Carman (permeability) equations, calculation of the flow rate of the membrane;
- **<u>Validation of the methodology</u>** with similar published experimental findings.

4.Theoretical calculations

5. Input data for modelling

Obtaining necessary parameters of <u>waste engine oil samples during 2012-2013</u>

#	Car and lubricant brand	Type of a car	Car ID #	Oil mileage	Viscosity, 100 °C, mm^2/s	Density, kg/m^3	
						Each	Average
1	MAN with 'Prista Ultra, 10W-40' lubricant	Dump truck	10 206 QAA	0 km	14.18	855.92	861.786
				5734 km	13.66	858.41	
				13172 km	14.73	862.23	
				25789 km	14.6	864.20	
				32789 km	13.1	868.17	
2		Bitumen tank wagon	10 207 QAA	0 km	13.94	855.92	857.898
				6015 km	13.96	856.51	
				14664 km	14.89	859.02	
				21498 km	14.4	858.78	
				33168 km	14.0	859.26	
3		Container truck	10 248 LAA	0 km	13.94	855.92	860.766
				6017 km	14.1	860.59	
				10587 km	14.1	859.15	
				16042 km	14.3	863.55	
				22283 km	14.1	864.62	

5. Inorganic (metal-ceramic) membrane production

Scale reduc-tion → Grinding → Sieving → Batch preparation → Compac-tion (com-pression) → Sintering → Second (final) compaction → Product final test

The procedure of tubular ceramic-metal membrane (based on **82% of electrocorundum, 14% clay and 4% of borosilicate concentrate**) preparation flows as below:

- Preliminary grinding of clay and borosilicate concentrate;
- Raw materials are blended in wet condition inside ball mill during 30 minutes while slip (slurry) has humidity of 45-50%;
- Finished slip is dried on pallets inside electric drying chamber;
- Dried mass passes through a gasoline and then through a sieve with cell size of 1 mm;
- Obtained powder is mixed with methylcellulose and water solution to obtain wet powder.
- The maximum moisture of the powder must be 17 to 19%;
- The mass is aged during one day and then processed inside vacuum auger (**the depth of vacuum is between 0.96 and 0.98 MPa**);
- Following the vacuuming of the mass, the vertical plunger (piston) press takes place for extrusion of tubular substrates. **The unit pressure of extrusion comprises 6-10 MPa;**
- Formed tubular goods are then subjected to air-seasoning in warm places for 2 days;
- **Maximum temperature of calcination following this storage must be 1200ºC.**

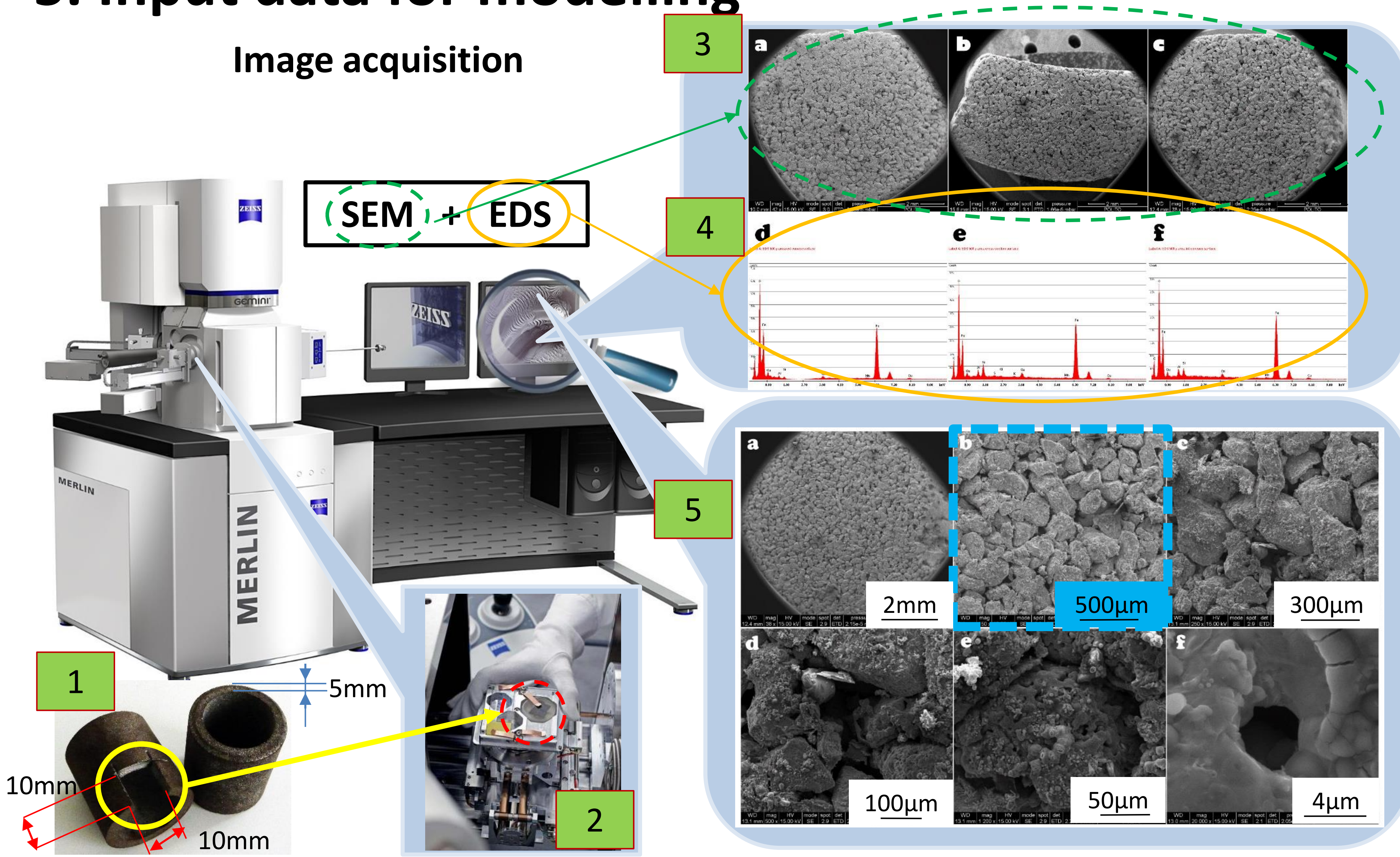
5. Input data for modelling

Requirements on image acquisition

- The surfaces of the membranes must **be orthogonal**;
- The membrane structure must **be homogeneous**;
- They (membranes) **must be produced based on sintering, pressing and/or extrusion**;
- The structure must **be granular**;
- The **structure** is basically **irregular**;
- In order to evaluate the membrane volumetric porosity, the membrane **images must be sliced** and the **slices must illustrate three different surfaces** – or three axes;
- In case if slicing is impossible or unavailable like in this work, then to have images from **three different surfaces**. In this work, this was like **internal, external and cross-sectional surfaces**;
- If even this is unavailable (like the case with validation – the only **single SEM image was available**) then **to use the declared volumetric porosity** value and use SEM image only for average pore size evaluation.

5. Input data for modelling

Image acquisition



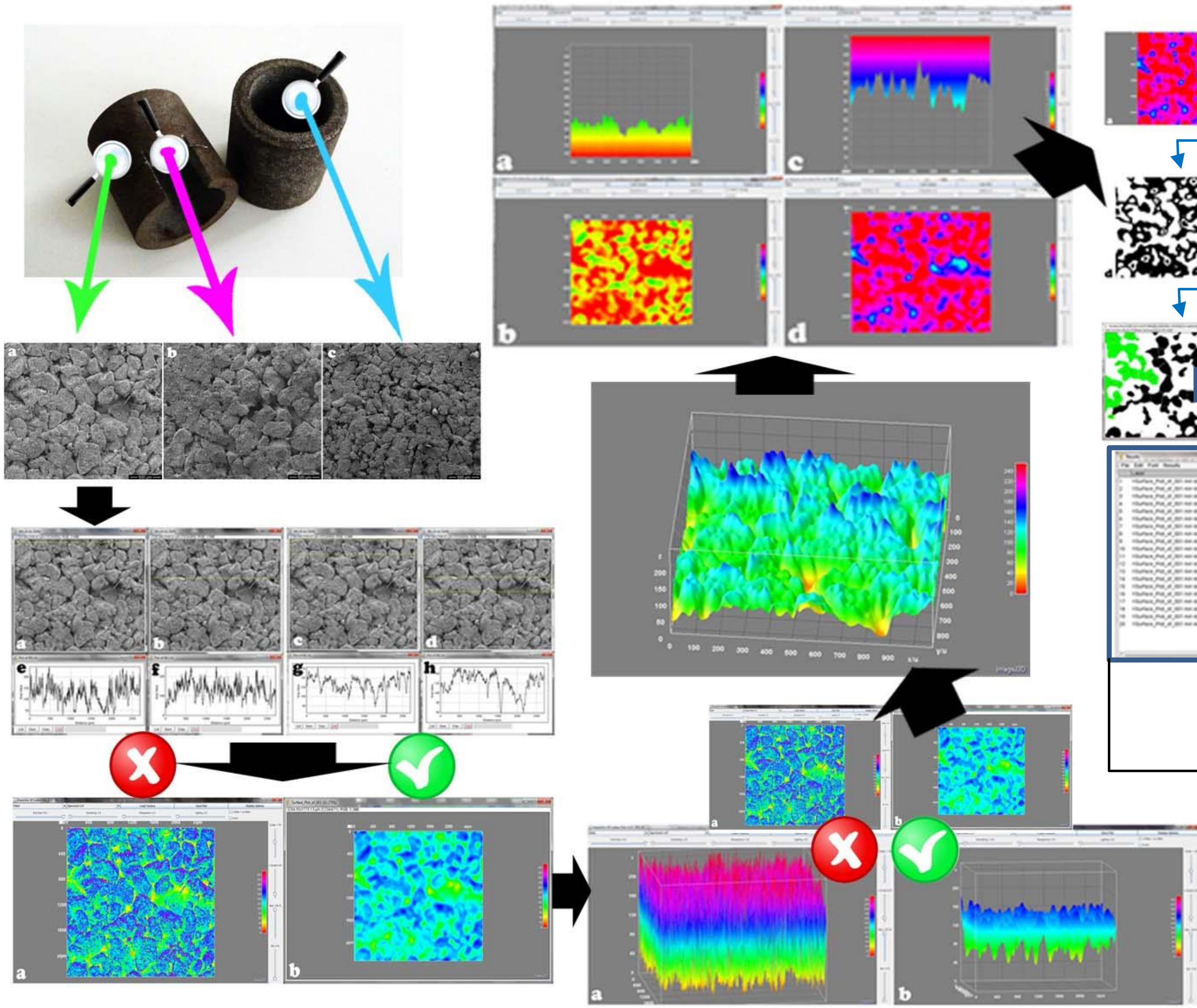
5. Input data for modelling

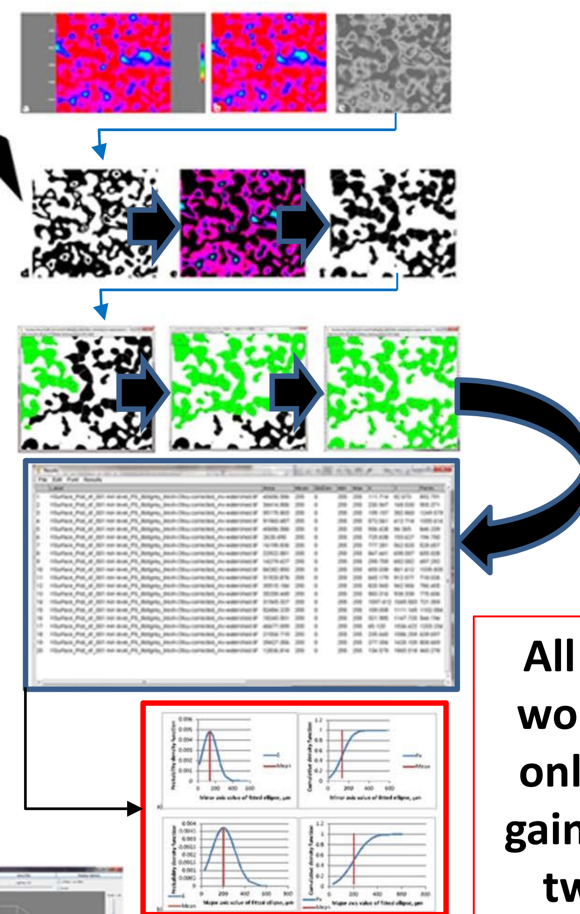
Image processing procedure

- **Depth analysis** of the membrane structure;
- Image **noise reduction**;
- **Reconstruction** of the 3D morphology;
- **Separation** of the recreated 3D morphology;
- **Cropping** obtained image to select the region of interest;
- **Calibration** of the size;
- **Converting** color image to grey level (one of the step to gain binary image);
- **Conversion** of grey level image into binary by thresholding algorithm;
- **Watershedding**;
- Application of **Boolean operators** on thresholded images;
- **Measuring (with software)** the porous and granular areas.

5. Input data for modelling

Image processing



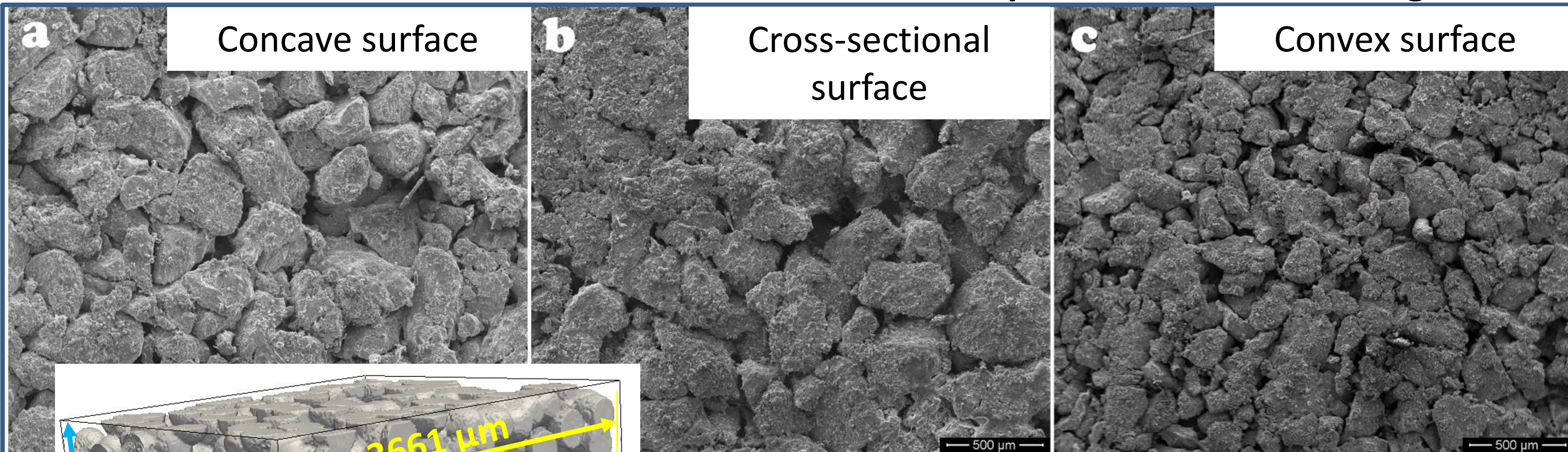


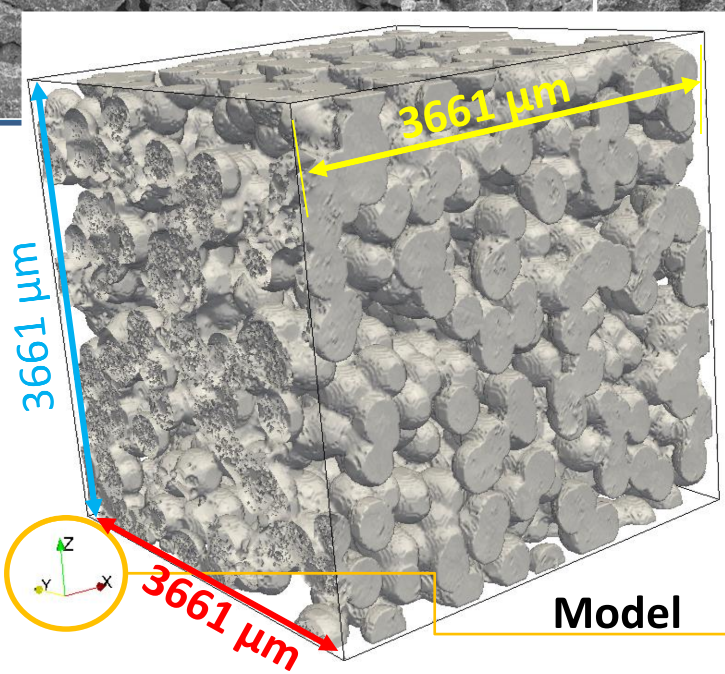
All the work is only to gain this two:

1. ***Volumetric porosity;***
2. ***Average pore size.***

6. Modelling

Membrane's 3D structure reconstruction and comparison with SEM images





Model

Membrane was reconstructed based on data given below which were obtained from image processing:

1.**Porosity: ε = 46%** 2.**Avg. grain size: D_g = 304 μm**

3.**Average pore size fitted with ellipses:**

D_{major} = 277 μm;
D_{minor} = 484 μm.

Actual

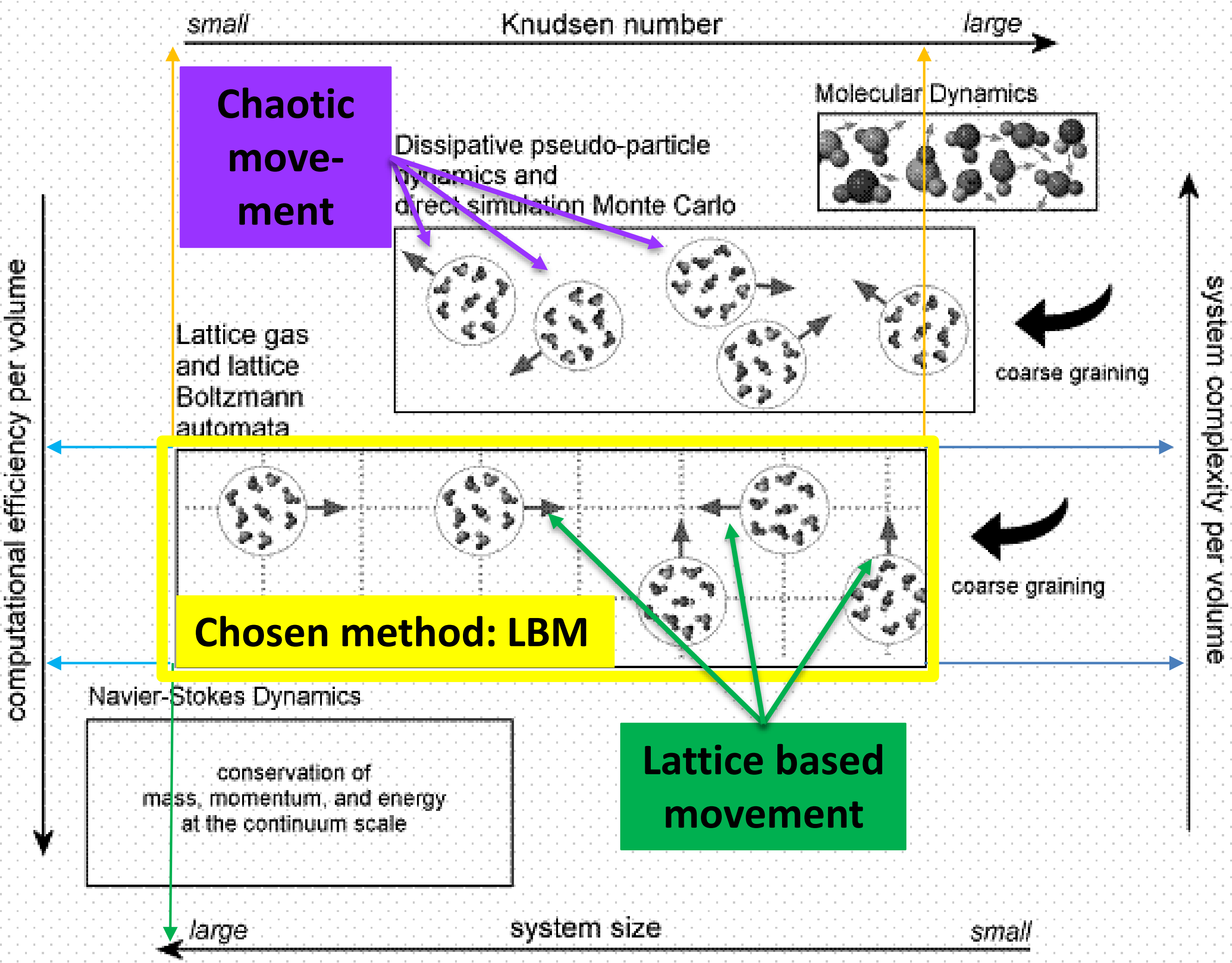
Clusterization or agglomeration was not considered.

Given sizes are: X*Y*Z=256X*256Y*256Z

Or X*Y*Z=3660.8 μm *3660.8 μm *3660.8 μm

6. Modelling, cont-ed

CFD: Bhatnagar-Gross-Krook (BGK) model



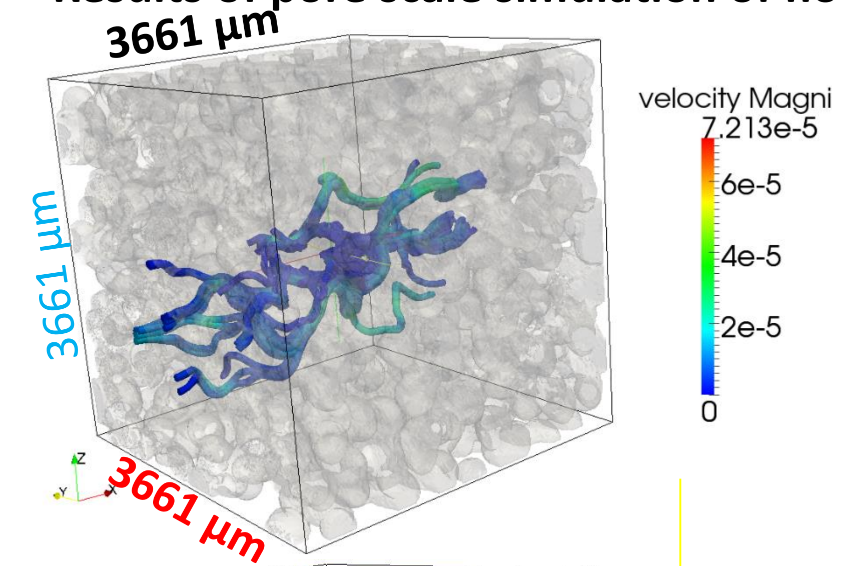
[Raabe, 2014]

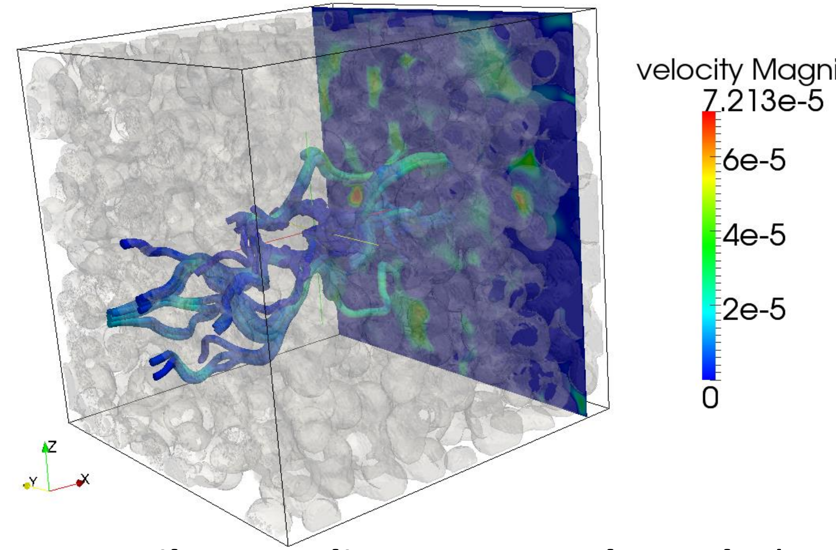
Advantages of LMB method compared with other CFD methods:

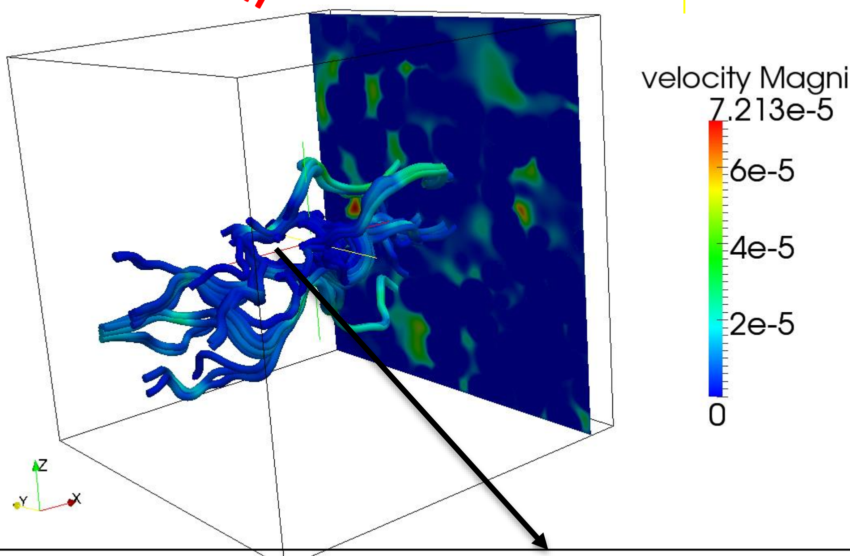
- Possibility to deal with **irregular morphologies**;
- Being **mesoscopic**, it bridges micro physics with macro;
- Possibility of **parallelization** of the computation;
- **Bounce-back principle** – reproduces the non slip boundary condition**.**
- There is **no need for complex mesh** generation – the is based on method **rectangular mesh**;
- Unlike to conventional CFD solvers, the LBM solves Boltzman equation, forcing relaxation parameter tend to zero

6. Modelling, cont-ed

Results of pore scale simulation of flow through reconstructed porous medium







Waste oil streamlines passing **through** the **structure of the membrane**.

Assumptions:

- Incompressible single phase fluid;
- Const. pressure and const. temperature;
- No slip boundary condition;

Initial input parameters:

- Fluid: viscosity & density;
- Membrane: avg. pore size & porosity.

Streamlines show that tortuosity of the membrane is rather big.

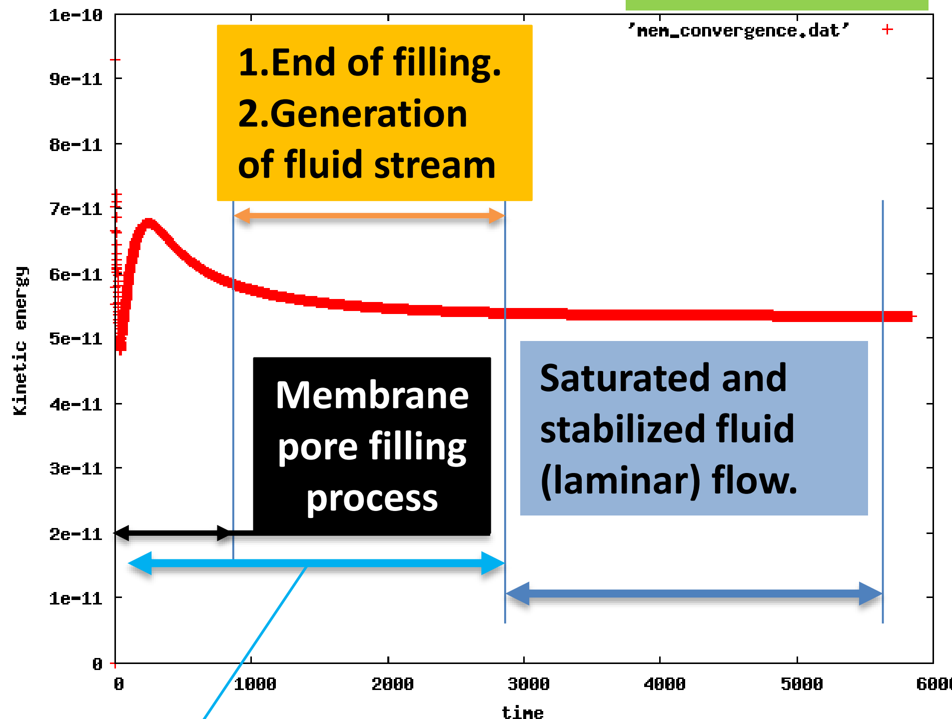
6. Modelling, cont-ed

Conventional filtration

Computational fluid dynamics

In this image, the convergence of membrane under the waste engine oil flow is given. As the CFD method of the study relies on LBM, the **The simulation physical time** comprised two days or **48 hours** which is equal to **5880 iterations** as given in the image.

The **flow saturation** occurs **between 2000 – 3000 iterations** and the flow inside the membrane becomes **stabilized** or **laminar**.

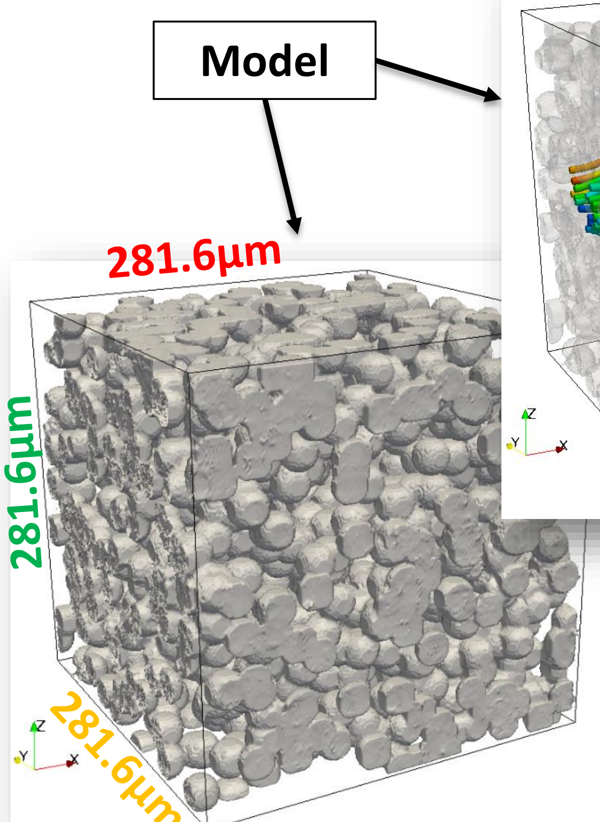


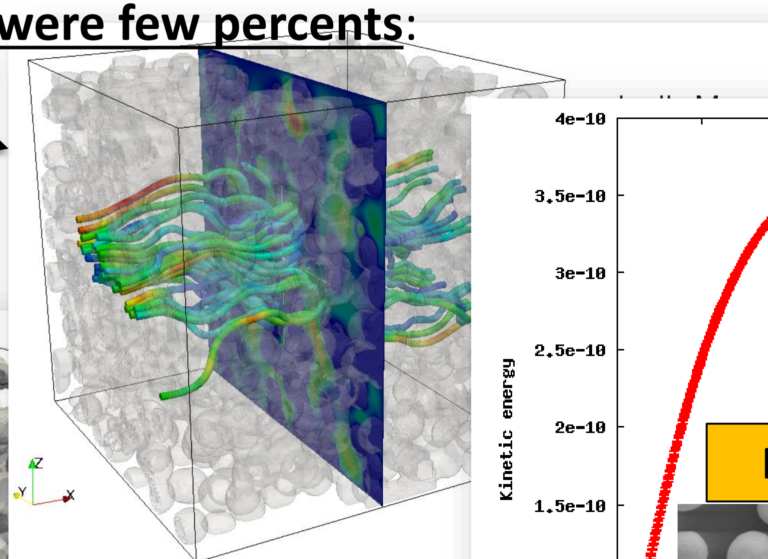
The **laminar flow coincidence proves** the primary assumption to apply **Darcy's law** and the calculation of the lubrication system flow. Precisely the flow at the outlet of the lube pump and inside the membrane.

In this region, error of the method is maximum!!!

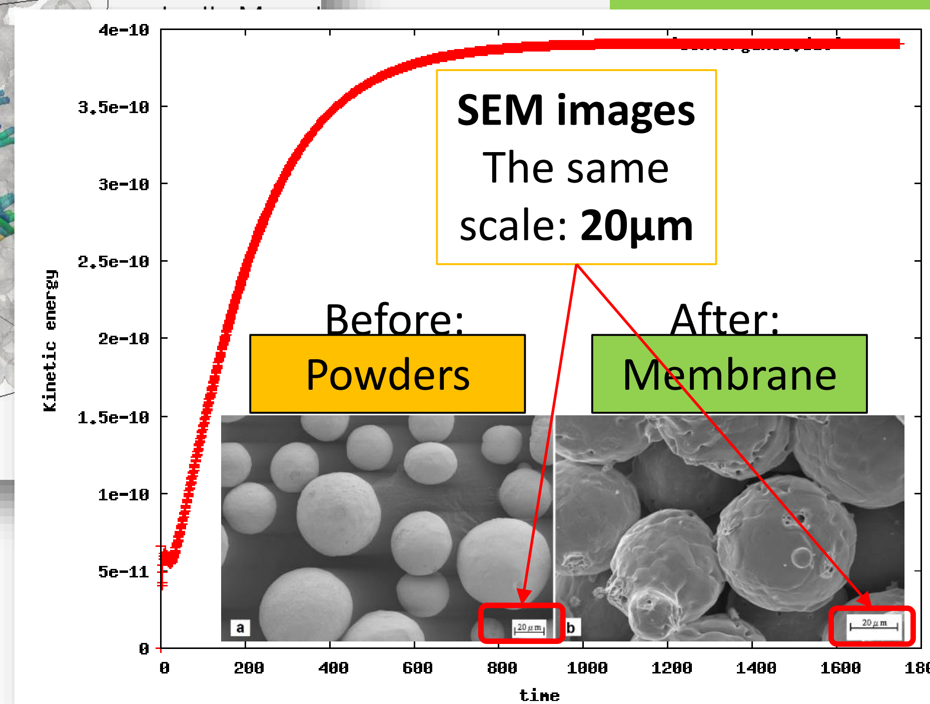
7. Validation of the method

The **validation** of the method is **necessary to know the possible error or difference between experimental and numerical results**. In this study, the same work has been accomplished. The study of Hwang (2009) had the appropriate finding necessary for validation. Declared porosity - 38%, fitted pore size - 39.6µm and 23.0µm and grain size ≈ 30µm, **error between experimental ($4.50*10^{-12}m^2$) and numerical ($4.92*10^{-12}m^2$) permeabilities were few percents**:





Microfiltration



8. Results of pore scale modelling and theoretical prediction

#	Parameters	Values	Units
1	Used computer (cluster) Transtec HPC: Total virtual cores/Total RAM/Nodes, [20]	72 / 144 / 8	Pcs/GB/pcs
2	Quantity of processors used for computation by PALABOS open source software	20	CPUs
3	Membrane porosity, ε	0.46	No unit
4	Flow velocity, u	0.00825	m/s
5	Reynolds number for flow in porous media, R_e^*	0.3318	No unit
6	Membrane permeability, k	$1.65*10^{-10}$	m^2
7	Geometric factor of the membrane structure (depending on the powder and process used and the resulting effective pore length, pore surface roughness tortuosity of the pore structure): function of shape, function of size, specific surface, degree of compression, function of topology, porosity parameter (macroscopic parameter)	187.14 (this study) 180 (for spherical grain shapes) 150 (Ergun) 250 (Hwang, 2009)	No unit
8	Membrane surface area for separation, A: A_1, (when membrane length is 40 mm, h=5 mm, d_{int}=25 mm)* A_2, (when membrane length is 251 mm, h=5 mm, d_{int}=70 mm)**	 0.00314 0.05517	m^2
9	Flow rate of the waste oil while passing the membrane, Q:		m^3/s
10	Case 1 - sizes of investigated membrane - ΔP100, A_1 - ΔP200, A_1 - ΔP300, A_1	- $0.9*10^{-3}$ - $1.8*10^{-3}$ - $2.7*10^{-3}$	m^3/s
11	Case 2 - sizes of real membrane by Henry Technologies, Model s4005 - ΔP100, A_2 - ΔP200, A_2 - ΔP300, A_2	- $15.9*10^{-3}$ - $31.8*10^{-3}$ - $47.7*10^{-3}$	m^3/s

* - sizes of the membrane under investigation; ** - estimated and available sizes

8. Results, cont-ed

1. Main finding of the study is that the membrane under 100kPa pressure drop, 100^{o}C and with the given internal 25mm, external 35mm diameter, 40mm length can produce or treat waste engine oil (with 817.2 kg/m^3 density and 14 cSt kinematic viscosity) with **0.3 ml/h flow-rate**!!!

2. The lubrication system needs at least flow-rate of 17 l/h. However, it worth to note that this flow-rate is produced with another size of the membrane and another type of material: length is 251mm, membrane thickness 1mm and internal diameter of 70 mm. Moreover, as that material is corrugated, filtration area is increased for several orders than of inorganic tubular one.

3. Membrane thickness is one the most important factors. The smaller the thickness – the better the permeability according to Kozeny-Carman permeability.

4. The geometric shape factor that is 187.14. In case of theoretical Kozeny-Carman for spherical grains, it was **180** and Ergun declared it to be **150** regarding his experimental findings. Hwang (2009) had **250** for spherical grains. Hence the factor seems to be in good agreement with theoretical one being **fitted** with **ellipsoid pores** and **spherical grain fitting**.

9. Conclusion

1. Waste oil in terms of oil contamination at microscale has been investigated.
2. Micro-morphologic model of the metal-ceramic material based membrane has been developed.
3. Optimal design of filtration has been proposed.
4. Reliable algorithm for reconstruction of the membrane filter morphology has been elucidated.
5. Developed morphological model has been approved by validating with experimental data from literature.
6. Optimal parameters for specific filtration process based on waste metal particles are proposed.
7. Geometrical shape factor is in good agreement with theoretical.
8. Recommendation for in-situ application of the membrane.
9. The method is valid for application down to 20 microns.
10. Depending on the contaminant size distribution, the membrane can be adopted (tuned) for full flow filtration.
11. For by-pass flow filtration, the membrane must have maximum 5 microns of pore diameter.

10. Recommendations

Practical application	1. Application in new material investigation; 2. Application of the results in production of improved membrane material; 3. Application of the results in separation: food production, beverages, and so on; 4. Application of the results in treatment: water, oil, etc.;
Theoretical	1. The membrane investigated **lacks of flow-rate** to be full-flow filter. It is better to use it as **bypass flow filter** instead. However, the grain and average pore sizes must be much smaller, not 200 or 300 microns, but 1-10 microns at most (the study of Hwang could be good reference in preparation at such scale sizes); 2. **The sizes** (length, internal diameter, etc) of the membrane **need to be enhanced** and thickness is decreased for this in-situ application. This will further allow to increase the filtration area; 3. The membrane surface must be increased to increase the flow rate. 4. **Further studies on tortuosity are suggested**. 5. **It is recommended to produce membrane with bigger porosity values but within the limit of 60-70%**; 6. The Kozeny-Carman curve of the membrane is desirable to construct following the production of the membranes with different porosities to understand critical values of the porosity for the given membrane material.

11. Acknowledgements

- Sincere acknowledgements of mine to Prof. F.Chiampo and Mr. M. Raimondo from Department of Applied Science and Technology (DISAT -Dipartimento Scienza Applicata e Tecnologia)

- I am acknowledged to Prof. F. Lombardi and the project Project Manu M5 for providing financial support in supporting this work;

- Many thanks for Hexagon Metrology Spa for their aid to be able to finish this study;

- Cordial acknowledgements to Uktam Salomov for his enormous help in this study, for the returning me back during my desperate times, for help in redrawing the plan in smooth way towards project success. My sincere acknowledgement of thanks to the Department of Energetics (DENERG) for computational aid and let us finish the work on time;

- Turin Polytechnic University in Tashkent (TTPU) is another supporter of this project not only financially but also technically. Deepest thanks to TTPU for such an opportunity.

12. References

1. M. Singh, K.K. Mohanty, “Permeability of spatially correlated porous media”, Chemical Engineering Science, 55, 5393-5403, 2000

2. K.S. Hwang, Y.J. Lin, "Effects of Powder Shape and Processing Parameters on Heat Dissipation of Heat Pipes with Sintered Porous Wicks," *Materials Transactions,* vol. Vol. 50, no. No. 10, pp. 2427-2434, 2009.

3. M. Neale, Lubrication and reliability Handbook, Butterworth-Heinemann, 2001.

4. S. Chun, "Network analysis of an engine lubrication system," *Tribology International,* vol. 36, pp. 609-617, 2003.

5. US Army Course Manual, *Principles Of Internal Combustion Engines,* Edition 8 ed., Subcourse Od1619, 2011, p. 100 pages.

6. K. Sharipov, "New technological principles of waste tractor oils regeneration in case of The Republic of Uzbekistan (in Russian)," Tashkent Automobile and Road Construction Institute, Tashkent, 2005.

7. T. Mang, W. Dresel, Lubricant and lubrication, 2nd Edition ed., Wiley, 2007.

8. F. Audibert, Waste Engine Oils: Re-refining and Energy Recovery, Elsevier, 2006.

9. European Commission IPPC Bureau at the Institute for Prospective Technological Studies, "Reference document on best available techniques for the waste treatments industries," Integrated Pollution Prevention and Control, 2006.

10. K. Mollenhauer, H. Tschoeke, Handbook of diesel engines, Springer-Verlag, 2010, p. 636 pages.

11. M. Rhodes, Introduction to Particle technology, 2nd Edition ed., Wiley, 2008, p. 450 pages.

12. PALABOS related publications," [Online]. Available: http://www.palabos.org/software/publications.

13. "ImageJ software homepage," NIH, [Online]. Available: http://rsbweb.nih.gov/ij/.

14. M. Singh, K.K. Mohanty, Permeability of spatially correlated porous media, *Chemical Engineering Science*, Vol. 55, pp. 5393-5403, 2000

15. D. Raabe, "Overview on the Lattice Boltzmann Method for Nano- and Microscale Fluid Dynamics in Material Science and Engineering," Max-Planck-Institut fur Eisenforschung GmbH, [Online]. Available: http://www.mpie.de/index.php?id=1208. [Accessed 15 01 2014].

16. Hasan A. Nooruddin, M. Enamul Hossain, Modified Kozeny-Carman correlation for enhanced hydraulic flow unit characterization, *Journal of Petroleum Science and Engineering*, Vol. 80, pp. 107-115, 2012

17. X. He, L.S. Luo, Lattice Boltzmann Model for the Incompressible Navier-Stocks Equation, Journal of Statistical Physics, Vol. 88, Nos. ¾, 927-944, 1997

18. ASM International Commette handbook, Friction, Lubrication, and Wear Technology, Vol.18, 1879 pages, 1992

19. M. El-Fadel, R. Khoury, "Strategies for vehicle waste-oil management: A case study," Resources, Conversation and Recycling, vol. 33, pp. 75-91, 2001.

20. Cluster ID webpage: http://staff.polito.it/pietro.asinari/energrid/energrid_cluster.html

21. Waste oil generation in Europe in 2006: http://ec.europa.eu/environment/waste/oil_index.htm

22. Annual waste oil generation in USA: http://toxics.usgs.gov/highlights/waste_oil.html

Thank you for your attention and please questions …