Suitable pulp grades for preparing nanofibrillated cellulose

Tiemo Arndt, Papiertechnische Stiftung
Valerie Meyer, Centre Technique du Papier
Ulf Germgård, Karlstad University

SUNPAP Workshop 5.10.2011

Outline

- Introduction and objectives
- Material and methods
- Results
- Conclusions
- Acknowledgment

Introduction and objective

- The technical challenges of preparing NFC using industrial scale techniques and the currently high costs of producing NFC limit the acceptance of NFC on the market.

- One important factor in this sense is that the fibre structure itself and consequently the pulping and bleaching conditions used have a major impact on the ability to produce NFC with a minimum amount of energy.

Introduction and objective

- Many studies are known which deal with the pulp pre-treatment and its influence on the energy composition
- It is obviuosly that depending on the decomposition in the pre-treatment stage the energy consumption in final homogenization stage can be reduced to a great extend by using for example a chemical pretreatment (e.g. TEMPO-oxidation) or an enzyme pretreatment.
- In most cases today is NFC produced from dissolving spruce pulp and the price of dissolving pulp is now about 2.5 times the corresponding price for conventional kraft pulp.
- Why is one pulp suitable for preparing NFC while another is not?

Material and methods

General approach

Market pulps of different chemical compostion

Laboratory pulps cooked to defined composition

Analysis of chemical composition

Mechanical-enzymatical pre-treatment

Morphological fibre properties, refining energy

Homogenization to MFC by a Microfluidizer M-110EH with a 200 µm chamber

SEM and light microscopic images

Preparation of MFC in according to Pääkko et al. Biomacromolecules, 8 (6), 1934-1941.

Materials and methods

- Chemical composition were analyzed by following methods
  - Intrinsic viscosity and LODP
  - Carbohydrate composition were determined using anion exchange chromatography /1/
  - WRV
- Fibre morphology were analyzed by using
  - MorFi analyzer (refined pulps)
  - Light microscopic images (MFC)
  - Scanning electron microscopy (MFC)

/1/ Hausalo, T. 8th International Symposium on Wood and Pulping Chemistry, Helsinki, Finland, 6-9 June, 1995, Vol. III, p 131-136 .

Materials and methods

- Market pulps

Pulp Reference	Pulping	Wood source	ISO brightness [%]	Limited viscosity number [ml/g]
A	Dissolving pulp	Pine / spruce	> 91	550
B	Paper pulp	Spruce / pine	> 89	820
C	Paper pulp	Birch	> 89	760
D	Dissolving pulp	Eucalyptus	> 91	435

Materials and methods

- Laboratory cooked and bleached pulps based on mill spruce chips

Pulp Reference	Prehydrolysis	Cooking	ISO brightness [%]	Limited viscosity number [ml/g]	Kappa number target
E	Yes	Kraft	87	909	30
F	Yes	Soda + AQ	84	782	30
G	No	Kraft	85	964	30
H	Yes	Kraft	87	863	20

- 320 g chips/ 2,5 l autoclave. Pre-hydrolysis were done in water at 1 h 160°C after ramping from 90°C with 1°C/min . The autoclaves were then cooled, opened and new cooking liquor was added. Finally, new ramping to 160°C using time as control variable.

- Bleaching was done as chlorite delignification in according to “Chlorite delignification of cellulosic materials” Useful method G..10 U. Reissued in May 2005 by PacTac, Canada”

Materials and methods

Market pulps

- Mechanical enzymatical pre-treatment
  - Pre-refining with a 12“ pilot-disc refiner to SR 26-29
  - Enzymatical pre-treatment (Cellulase Novo 476)
  - Refining was continued until the highest drainage index was reached for each pulp without pulp darkening
  - Homogenization to MFC by a Microfluidizer M-110EH with a 200 µm chamber (5 passes)

Materials and methods

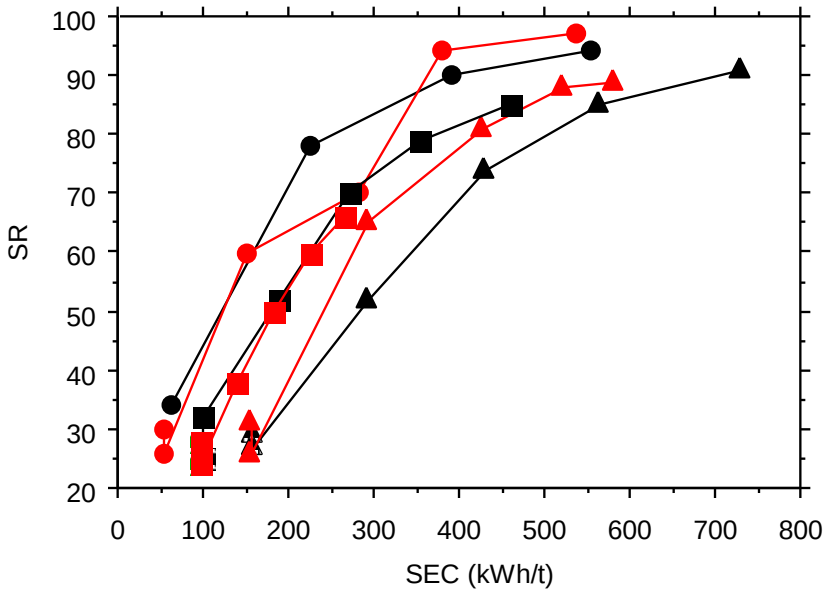
Laboratory cooked pulps

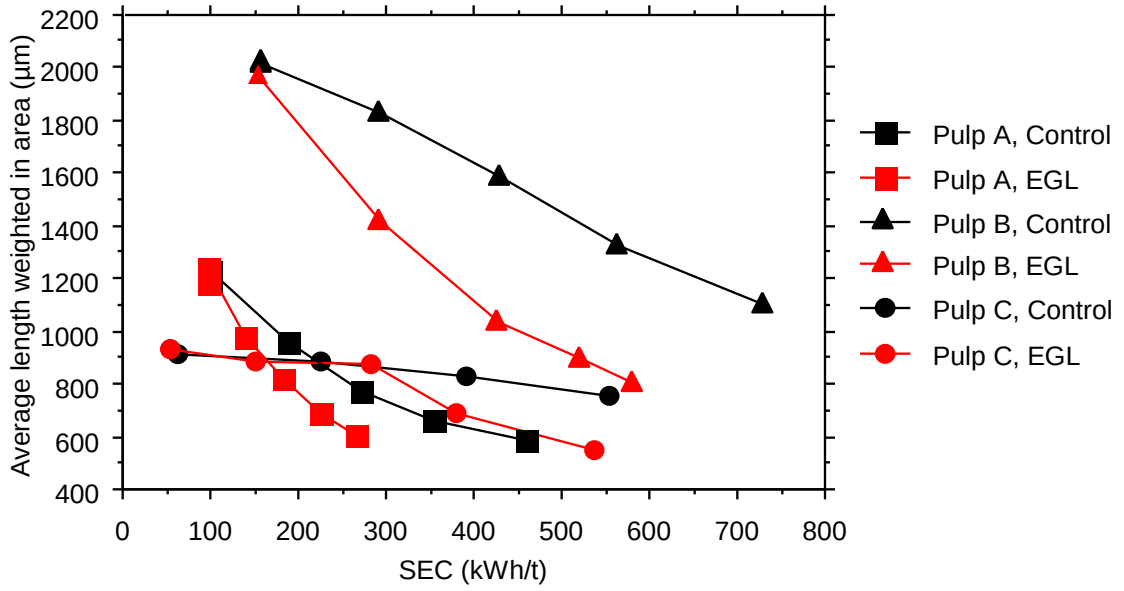
- Mechanical enzymatical pre-treatment
  - Refining was done in a Voith-Sulzer refiner to a target SR 18-23. (3.5% consistency, SEL 1.8 Ws/m, 140 kWh/t)
  - After the enzymatic stage (endoglucanase) the pulps were refined to a target SR-level of 80 (consistency 3.0%, SEL 0.9 Ws/m, SRE up to 620 kWh/t).
  - An additional laboratory refining was also performed with a Valley beater for 30 min, because the fibres were up to 2 mm long
  - Homogenization to MFC by a Microfluidizer M-110EH with a 200 µm chamber (5 passes)

Chemical composition of the market pulps

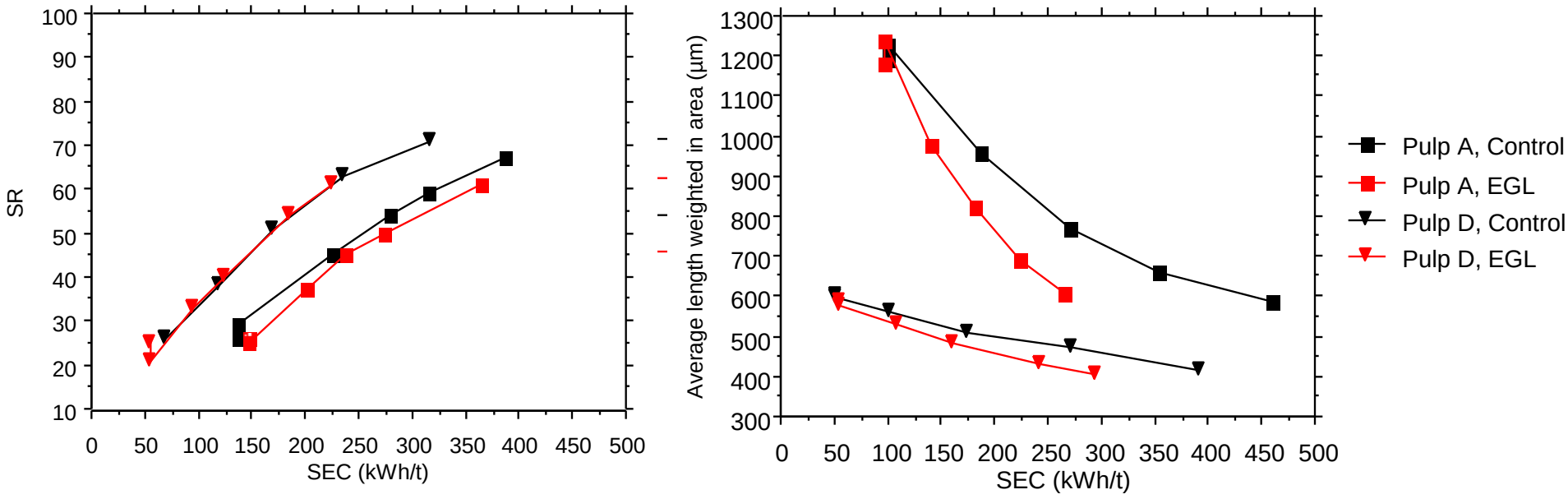
	Unrefined			
Property	**Pulp A - Diss. SW**	**Pulp B - Kraft SW**	**Pulp C - Kraft Birch**	**Pulp D - Diss. EUC**
Viscosity (cm³/g)	550	820	760	435
LODP (cm³/g)	123	123	171	120
WRV (%)	104	129	163	96
Galactose (rel %)	< 0,05	0.2	< 0,05	<0.05
Glucose (rel %)	96.5	85.5	74.9	96.9
Mannose (rel %)	2	5.7	0.6	0.8
Arabinose (rel %)	< 0,05	0.7	< 0,05	<0.05
Xylose (rel %)	1.5	8.5	24.4	2.2
L(w)c - Morfi (mm)	1.553	2.224	0.929	0.637
Fines(l)c - Morfi (%)	7.1	3.54	2.11	14.01

Refining response of the market pulps



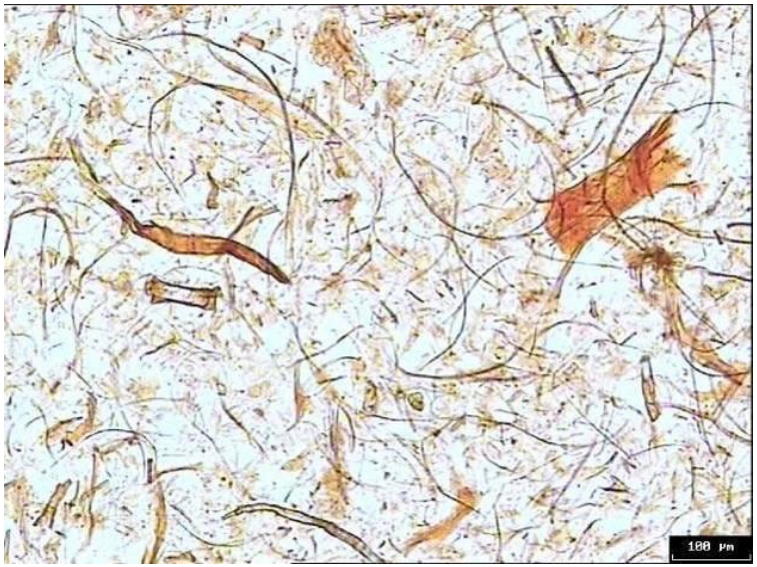


Refining response of the market pulps

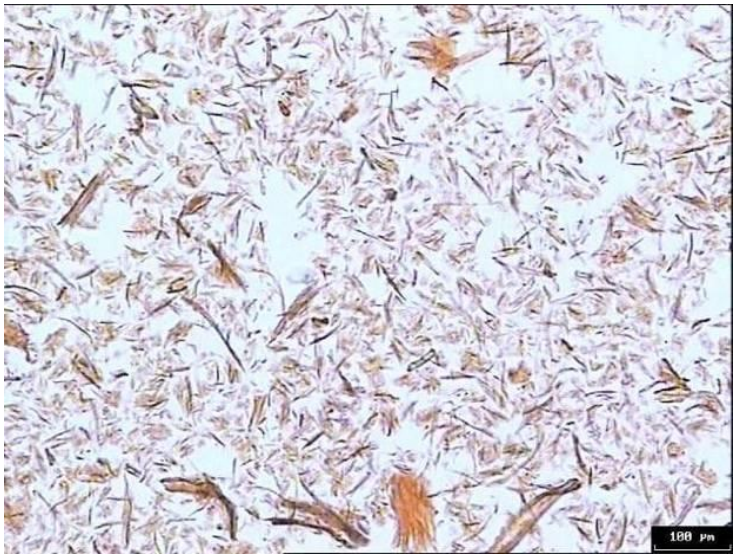


Light microscopic images of MFC
- market pulps -

Pulp A Diss. - no enzymatic pre-treatment

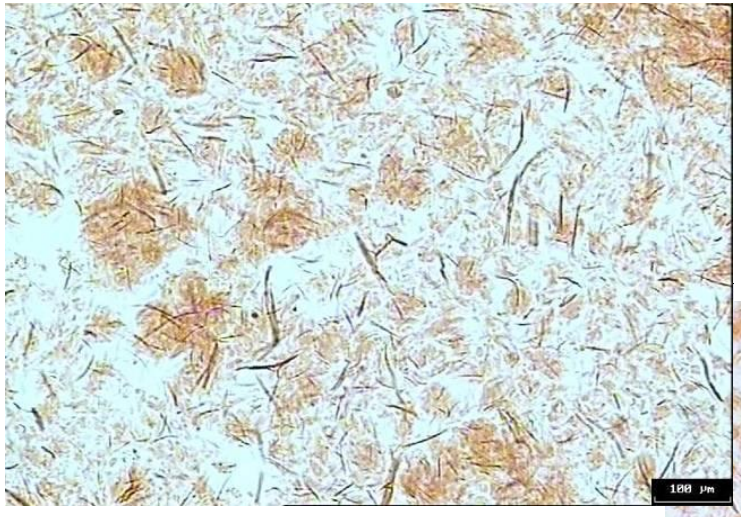


Pulp A Diss. – EGL pre-treatment



Light microscopic images of MFC
- market pulps -

Pulp B SW Kraft– EGL pre-treatment



Pulp C Birch Kraft– EGL pre-treatment

Pulp D Euca - EGL pre-treatment

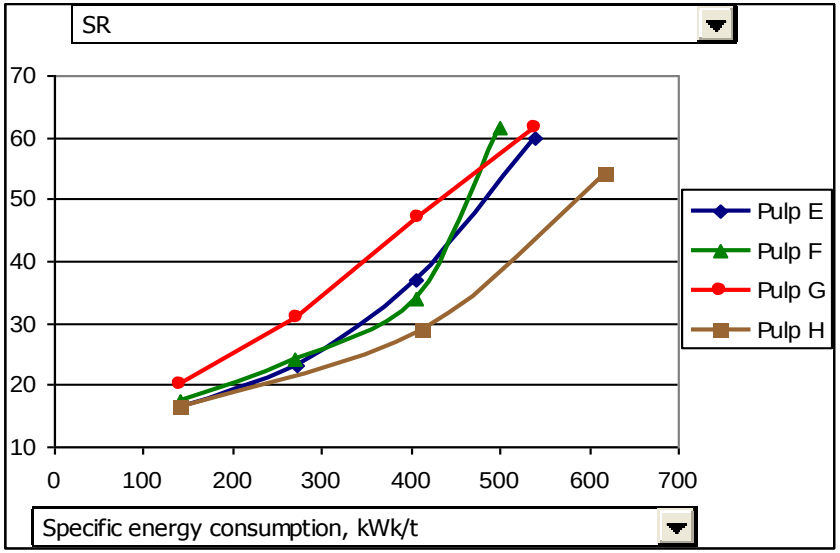
Conclusions for the market pulps

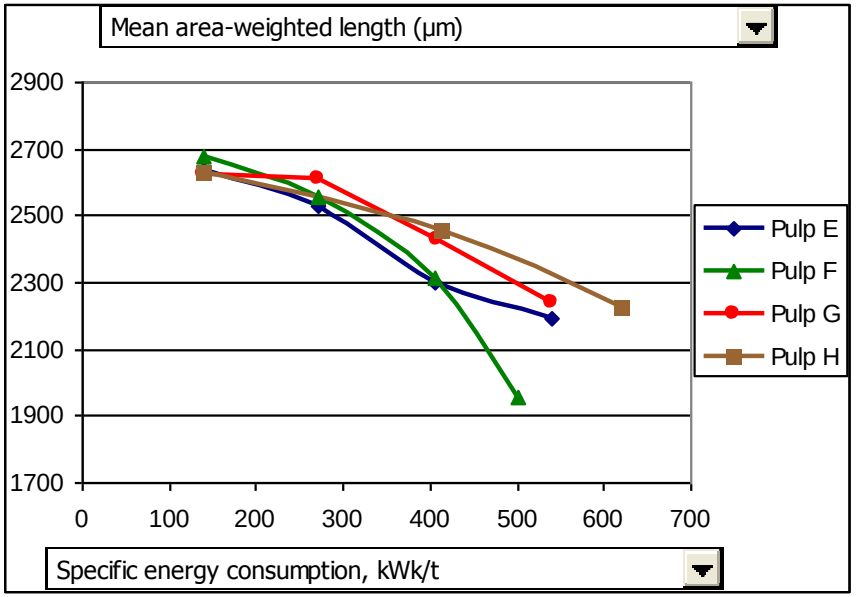
- The two dissolving pulps showed significantly lower energy consumption to reduce the fibre length to a minimum level before final homogenization compared to spruce/pine and birch Kraft pulps.
- The refining resistance were much slower of the dissolving grades as compared to the Kraft pulps.
- Based on these results in the laboratory different pulps with dissolving-like properties were cooked.

Chemical composition of the laboratory cooked pulps

	Unrefined					
	Pulp A - diss. SW	**Pulp D - diss. EUC**	**Pulp E**	**Pulp F**	**Pulp G**	**Pulp H**
	Market	**Market**	**Pre-H. / Kraft / κ 30**	**Pre-H. / Soda AQ / κ 30**	**Kraft / κ 30**	**Pre-H. Kraft / κ 20**
Viscosity (cm^3/g)	550	435	909	782	964	863
LODP (cm^3/g)	123	120	128	133	182	121
Galactose (rel %)	< 0.05	<0.05	0.1	0.1	0.3	0.1
Glucose (rel %)	96.5	96.9	94.2	93.6	84.7	94.3
Mannose (rel %)	2	0.8	2.4	2.7	7	2.4
Arabinose (rel %)	< 0.05	<0.05	<0.05	<0.05	0.6	<0.05
Xylose (rel %)	1.5	2.2	3.3	3.7	7.5	3.3
L(w)c - Morfi (mm)	1.6	0.637	2.71	2.68	2.71	2.71
Fines(l)c - Morfi (%)	6.76	14.01	1.08	0.95	1.04	1.14

Refining response of the laboratory cooked pulps

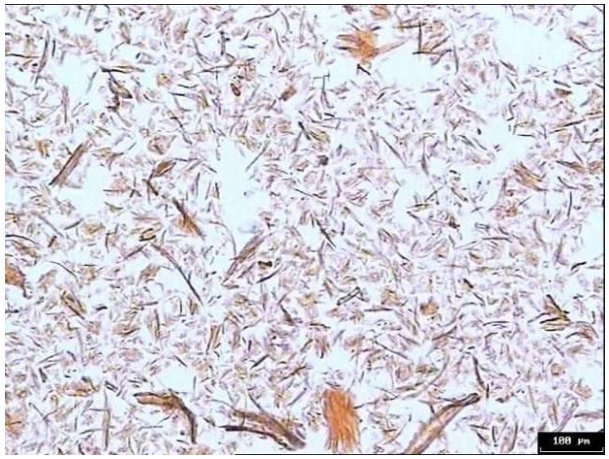




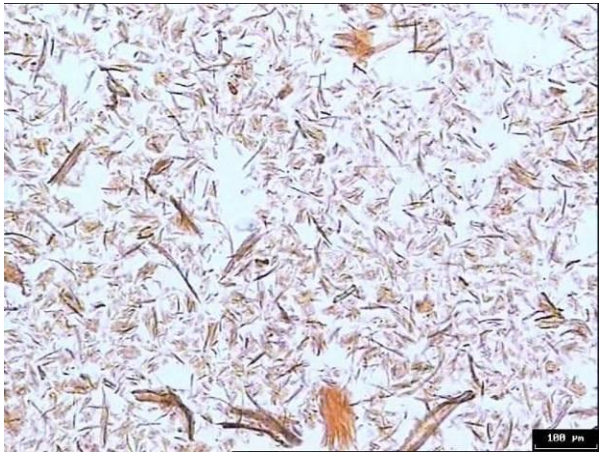
- The shown data are after refining with a conical refiner.
- In order to avoid clogging of the microfluidizer the pulps were again refined with a Valley Beater for 30 min to a fibre length 0.47 – 0.66 mm

Light microscopic images of MFC
- laboratory cooked pulps -

Pulp A – dissolving spruce

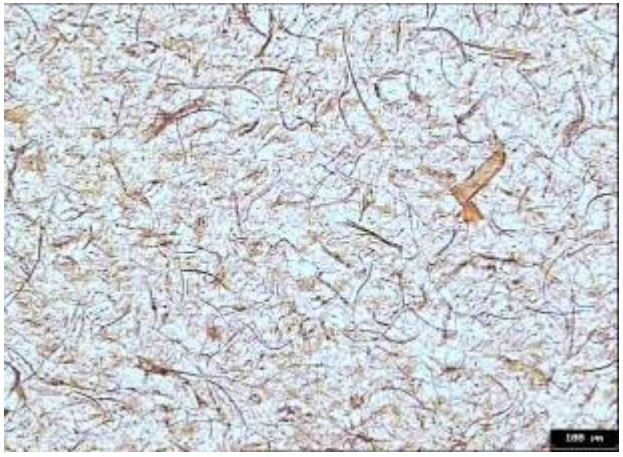


Pulp D – Diss. Euca

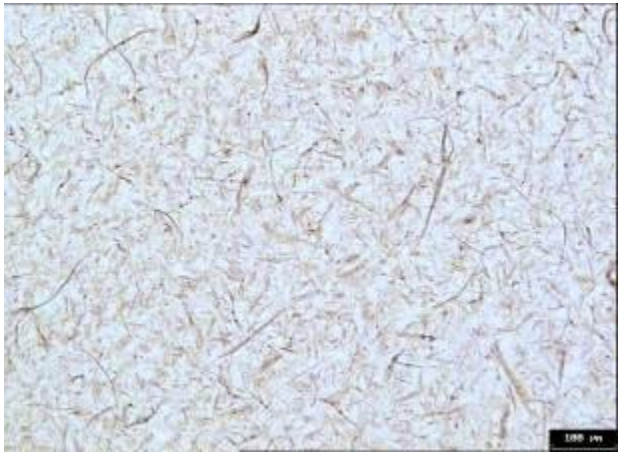


Pulp E – pre-hydrolysis - kraft cooking (kappa 30)

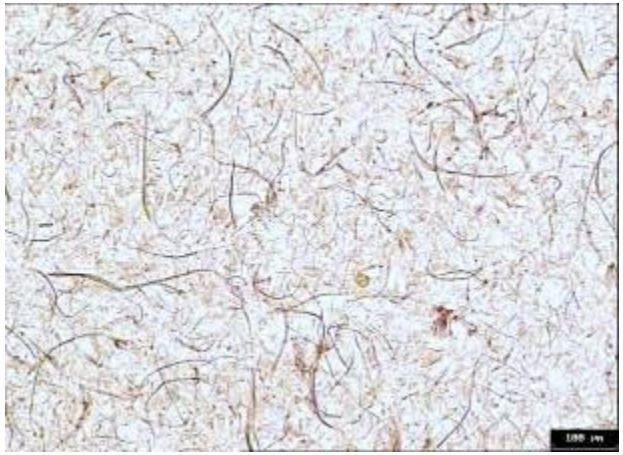
Pulp F - pre-hydrolysis - soda AQ cooking



Pulp G - conventional kraft

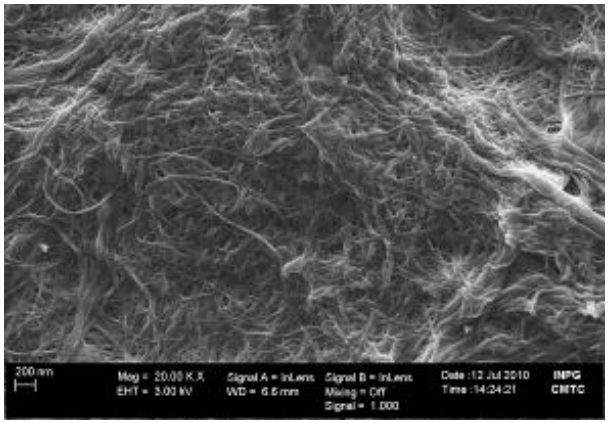


Pulp H - pre-hydrolysis kraft cooking (kappa 20)

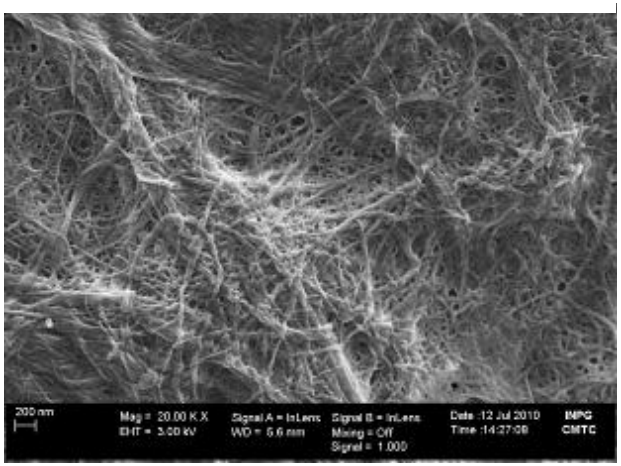


SEM images of MFC
- laboratory cooked pulps & market pulps -

Pulp B SW Kraft– EGL pre-treatment

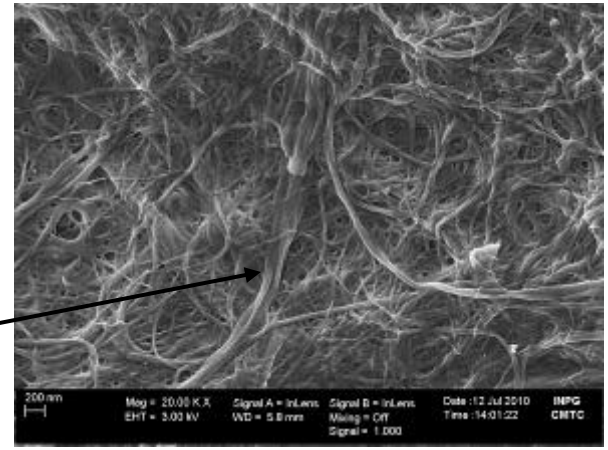


Pulp D Euca - EGL pre-treatment

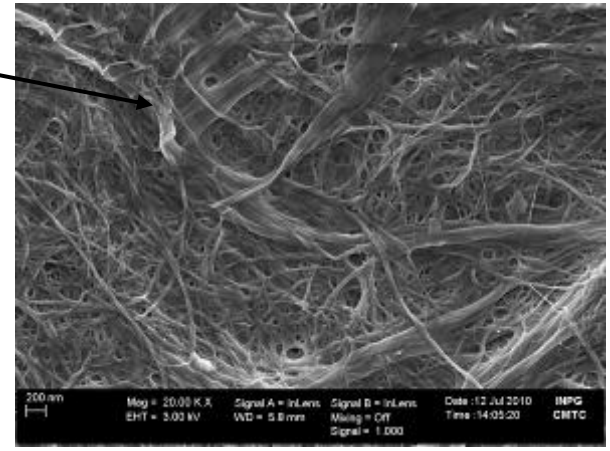


Diameter and thickness of the fibrils of the laboratory cooked pulps are higher

Pulp G - conventional kraft



Pulp H - pre-hydrolysis kraft cooking (kappa 20)



Conclusions laboratory cooked pulps

- The reduction in fibre length during refining of the laboratory cooked pulps were much more difficult as expected, even if the pulps had properties like dissolving pulp grades.

- Even if the chemical composition of the laboratory cooked pulps E, F, and H were close to dissolving market pulp properties, the morphology of the MFC particles looked completely different than the MFC suspensions prepared from the market dissolving pulps. It can be seen that the suspensions contained many more coarse particles and non-disintegrated intact fibre structures.

Why is one pulp suitable for preparing NFC while another is not?

Some speculations:

- From the literature it is known that the pulp pre-treatment had to the greatest extend influence on the energy consumption during NFC preparation, but also on the chemical structure of the NFC.
- Pulp cooking in the laboratory is gentler with respect to mechanical forces than mill cooking.
- It can only be speculated that the introduction of mechanical fibre wall damage during mill pulping was responsible for the lower energy requirements during post-refining and the more homogeneous structure of the MFC.
- If this assumption can be confirmed, future pulping strategies for preparing pulps suitable for MFC production can be easily introduced into existing Kraft pulping lines.
- In addition, this might also help to reduce the pulp raw material costs of MFC production since conventional Kraft pulps are always cheaper than dissolving pulps.

Acknowledgment

- The research leading to these results received funding from the European Community's Seventh Framework Programme under Grant Agreement No 228802.