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The Influence of Pulping Process and Energy Consumption on Properties of Nanofibrillated Lignocellulose (NFLC) Films Isolated from Wheat Straw

Utjecaj procesa proizvodnje pulpe i potrošnje energije na svojstva filmova na bazi nanofibrilirane lignoceluloze (NFLC) izolirane iz pšenične slame

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ABSTRACT • *The present research has primarily focused on the production of nanofibrillated lignocellulose (NFLC) instead of nanofibrillated cellulose (NFC), which could be produced with less energy and is expected to have similar uses as NFC, especially in the sectors where the transparency is not important. Furthermore, the effect of energy consumption needed for NFLC production and also the influence of pulping methods on the produced NFLC properties has been surveyed. Through mechanical refining and different passes in microfluidizer, the results showed the average diameter of NFLC declined from around 19000 nm to 36 nm. Soda-NFLC films had higher calliper and lower roughness, compared to those of MEA at given energy consumption in refiner and microfluidizer. For both kinds of pulps, the optimum level of energy consumption to reach the best tensile index of NFLC films was 258 kWh/t, with three passes through microfluidizer. More increase in the number of passes and pressure only resulted in increasing of energy consumption without any positive effect on improving the tensile index. The maximum tensile indices of NFLC films obtained from soda and MEA pulping processes were 113.5 and 119.86 N·m/g, respectively. The burst index of 8.5 kP·m^2/g and the energy consumption of 458 kWh/t were obtained for five passes through microfluidizer. With the increase of the number of passes of soda and MEA samples through microfluidizer, the opacity decreased but transparency increased.*

Keywords: *nanofibrillated lignocellulose; wheat straw; soda and MEA pulping; energy consumption*

SAŽETAK • *Ovo je istraživanje usmjereno na proizvodnju nanofibrilirane lignoceluloze (NFLC) umjesto nanofibrilirane celuloze (NFC). Ta bi se celuloza (NFLC) mogla proizvesti s manje energije i moglo bi se očekivati*

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da će imati sličnu uporabu kao NFC, osobito u područjima gdje transparentnost nije osobito važna. Ispitan je i učinak potrošnje energije potrebne za proizvodnju NFLC-a, kao i utjecaj metode proizvodnje pulpe na svojstva proizvedene lignoceluloze. Rezultati istraživanja pokazali su da je mehaničkim oplemenjivanjem i uz različit broj prolazaka kroz mikrofluidizator prosječni promjer NFLC-a pao s oko 19 000 nm na 36 nm. NFLC filmovi od natronske pulpe pri određenoj su potrošnji energije u rafinatoru i mikrofluidizatoru imali veću debljinu i manju hrapavost u usporedbi s onima od MEA pulpe. Optimalna razina potrošnje energije za postizanje najboljega vlačnog indeksa NFLC filmova za obje vrste pulpe bila je 258 kWh/t, uz tri prolaska kroz mikrofluidizator. Povećanje broja prolazaka i tlaka rezultiralo je samo povećanjem potrošnje energije bez ikakva pozitivnog učinka na poboljšanje indeksa kidanja. Maksimalni indeksi kidanja NFLC filmova od pulpe dobivene natronskim i MEA postupkom bili su 113,5 odnosno 119,86 N·m/g. Indeks prskanja od 8,5 kP·m^2/g i potrošnja energije od 458 kWh/t dobiveni su prolaskom pulpe kroz mikrofluidizator pet puta. S porastom broja prolazaka uzoraka natronske i MEA pulpe kroz mikrofluidizator smanjila se neprozirnost, ali se povećala transparentnost uzoraka.

Ključne riječi: *nanofibrilirana lignoceluloza; pšenična slama; priprema pulpe natronskim i MEA postupkom; potrošnja energije*

1 INTRODUCTION
1. UVOD

Nanotechnology can create an entirely new industry, while reducing the demand for some goods and increasing the demand for some other goods (Wegner *et al.,* 2009). With help of nanotechnology, lignocellulosic sector is capable to produce new high-tech products and create markets with a wide variety of applications. One of these new high-tech products is nanofibrillated cellulose (NFC) (Ankerfor, 2012). NFC is composed of nano sized cellulose fibrils with a high aspect ratio (length to width ratio) of more than 100. The development of NFC was pioneered by Turbak *et al.* in 1983.They demonstrated that, by treating wood-based cellulose fiber suspensions with a high-pressure homogenizer, a gel-like material can be produced (Turbak *et al.,*1983; Zimmerman, 2010; Spence *et al.,* 2011$_a$). The resulting material was denoted as Microfibrillated Cellulose (MFC) or Nanofibrillated Cellulose (NFC), and it showed promising properties and high potential to produce diverse industrial and commercial goods such as cosmetics, health, food, packaging, etc (Abdul Khalil et al., 201; Henrik *et al.,* 2008; Yousefi *et al.,* 2011; Spence, 2011).

Today, NFC is produced from various cellulosic sources among which wood is the most important source of cellulose and is the main raw material for NFC production (Iwamoto *et al.,* 2005; Spence, 2010; Habibi *et al.,* 2010; Afra *et al.,* 2013). Due to the increasing demand for wood in other industrial sectors and also the need to protect forests as one of most important factors in the fight against global warming and climate changes, appropriate alternatives to wood should be sought. Lignocellulosic agricultural residues are a major source as they are renewable, environmentally beneficial and also they need less energy consumption in the production of NFC and thus they could be a good substitute for wood as a raw material (Alemdra, 2008).

To liberate the cellulose from lignocellulosic matrix and produce NFCs, the lignocellulosic raw material must be fractionated. For this purpose, there are some delignification processes in industrial scale such as kraft, sulphite and soda pulping processes. Soda pulping is the dominant process for lignocellulosic agricultural residues. Strong alkaline cooking liquors in this process dissolve carbohydrates to a great extent. In addition, the capability of sodium hydroxides in dissolving lignin is restricted to some specific lignin structures. These conditions result in a pulp with low yield, low hemicelluloses content and high condensed lignin. In return, MEA pulping can dissolve lignin in a good selective way. It means that in comparison with soda pulp, MEA pulp has significantly higher yield, higher hemicelluloses and lower lignin contents (Hedjazi *et al.,* 2009; Salehi *et al.,* 2014).

To produce pure NFC, it was necessary to remove hemicelluloses and lignin by pre-extraction treatments and diverse bleaching sequences, because in principle, NFCs are produced with bleached cellulose fibers (dissolving pulp, white pulp). Bleaching process consumes energy and chemicals and imposes a lot of environmental pollution (Spence *et al.,* 2011). Recently, unbleached lignocellulose fibers (brown pulp) have been converted to nanostructures (Spence, 2011). The resulting materials can be referred to as nanofibrillated lignocellulose (NFLCs). From an environmental and economic point of view, because of less chemicals and energy needed to produce unbleached pulps, NFLCs are superior to NFCs (Yousefi *et al.,* 2018; Djafari Petroudy, 2014).

For NFC production, normally the pulp fibers had to be run several times through an apparatus like homogenizer and microfluidizer, which resulted in high energy consumption. Nowadays, the development of disintegration methods, which are less energy consuming, became a priority in NFC production. Thus, various mechanical pre-treatments have been suggested in order to obtain NFCs at lower energy input. Mechanical pre-treatments are arried out on the pulp to reduce fiber size and/or to pre-defibrillate the fibers, thus reducing the frequency of equipment clogging and the energy consumption during conversion of pulps to NFC (Spence *et al.,* 2011). Alternatives for mechanical reduction of fiber size include disk refiners, PFI mills and valley beaters. Gradual peeling off of the external cell wall layers (P and S1 layers) is carried out by a refining treatment prior to homogenization or micro-fluidization. Thereby, the S2 layer is better exposed to mechanical actions and causes internal fibrillation during homogenization and micro-fluidization (Andresen *et al.,* 2006; Henriksson *et al.,* 2008; Iwamoto *et al.,* 2005; Nakagaito and Yano, 2004; Spence *et al.,* 2011; Turbak *et al.,* 1983).

Unfortunately, the most important challenging issue of NFC production at industrial scale is its high energy consumption (Yousefi, 2011; Ankerfors, 2012; Spence, 2011b; Zimmermann, 2010; Eriksen, 2008). In general, energy consumption in NFC production differs significantly due to parameters such as source of lignocellulose, fractionation method of lignocellulose, number of passes and flow rate and cellulose fibers.

Nowadays many researchers are trying to find new ways to reduce production costs of NFC to obtain nanomaterials and nanocomposites at a lower price, as well as to increase industrial production capability (Ankerfors, 2012; Spence *et al.,* 2010; Spence *et al.,* 2011; Zimmermann, 2010; Paakko *et al.,* 2008; Syverud *et al.,* 2011; Iwamoto, 2009). Therefore, this research has focused on the study of the influence of simultaneous use of wheat straw as an inexpensive agriculture lignocellulosic residue, different pulping processes without bleaching as downsizing methods, and industrial simulated refiner treatment as mechanical pre-treatment on energy consumption and properties of produced NFLCs.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

Wheat straws were collected from cultivation areas in the north of Germany. Cleaned straw was chopped into small pieces by a cutter in length of 3-5 cm. The prepared samples were conditioned in a laboratory and stored in plastic bags. Before experiments, the moisture content of the material was determined by Tappi T 264-0m 88 standard. Analytical grade monoethanolamine (MEA) and NaOH, purchased from Baden Aniline Soda Factory (BASF, Germany) were used.

2.2 Methods
2.2. Metode

2.2.1 Chemical compositions
2.2.1. Kemijski sastav

The chemical composition of wheat straw was determined according to relevant Tappi test methods as follows: sample preparation (T267-om 85), ash content (T211-om 93), extractives soluble in alcohol-acetone (T207-om 97), cellulose content (T264-om 88), lignin content (T222-om 97) and holocellulose method; Useful method 249- um 75.

2.2.2 Pulp production
2.2.2. Proizvodnja pulpe

Soda and MEA processes were used for pulping wheat straw. In soda process, alkalinity of 16 %, cooking time of 30 min, temperature of 160 °C and liquor to straw (L/S) ratio of 3 to 1 were selected. In MEA pulping, cooking time of 45 minutes, cooking temperature of 145 °C and (L/S) ratio of 4 to 1 was employed. Pulping was performed in a15 l rotating digester equipped with indirect heating. At the end of cooking, the digester was cooled down and the pulp discharged into a sieve, thoroughly washed with tap water, disintegrated in a laboratory pulper for 5 minute and then screened on a vibrating 0.15 mm slot screen. The screened pulp was dewatered and stored in polyethylene bags at 4 °C until further processing. The pulp was drained and after measuring the moisture content of the pulp, the total yield, screened yield and screen reject were determined. After complete hydrolysis of the pulps, carbohydrates and simple sugars were characterized by 72 % sulfuric acid using HPLC. The following pulp properties were also determined: kappa number, (Tappi T 236-om 06), viscosity (Zellcheming-Vorschift IV 61/36) and brightness, (T 425-om 98).

2.2.3 Mechanical pre-treatment
2.2.3. Mehanički predtretman

For refining of pulp, the pilot refiner of Voith Company (LR 40) was employed. For refining purposes, 1500 gr pulp based on dry weight was added to the refiner at energy consumption of 170 kWh/t. This level of energy consumption in the refiner comes from preliminary test (Ahmadi, 2014).

2.2.4 Manufacture of NFLC
2.2.4. Proizvodnja NFLC-a

The refined soda and MEA unbleached pulp suspensions were mechanically disintegrated at 0.24 % solids content using a high-pressure fluidizer (Microfluidizer M-110EH-30; Microfluidics Corp., USA). In the standard procedure, the samples were passed two times through the large chambers and four times through the small chambers. Due to the narrowness of the chambers, operating pressures of approximately 69 MPa (10 kpsi), and 138 MPa (20 kpsi) are normally needed to push the material through the large and small chambers. After passing the chambers, the samples were cooled in a heat exchanger before they were collected in a jar (Ankerfors, 2012). Table 1 presents the energy consumption of microfluidizer in each pass. The microfluidizer energy measurements were 79 and 100 kWh/t per pass for processing pressures of 69 MPa (10 kpsi) and 138 MPa (20 kpsi), respectively.

Table 2 shows sample identification codes. Control sample refers to mechanically un-treated soda and MEA pulps.

2.2.5 Preparation of nanofilms
2.2.5. Priprema nanofilmova

The microfluidizer treated NFLC suspensions at 0.24 % consistency were first degassed for 10 min with a water vacuum pump. The degassed suspensions were then used to form nanofilms using a semiautomatic sheet former (Rapid-Köthen) under vacuum. The apparatus and procedure for film formation was adapted as described in a previous study (Glasenapp, 2014).

Table 1 Energy consumption of microfluidizer in each pass
Tablica 1. Potrošnja energije mikrofluidizatora pri svakom prolasku

Pass number *Broj prolaska*	**Microfluidizer chamber** *Komora mikrofluidizatora*	**Pressure, MPa** *Tlak,* MPa	**Energy consumption, kWh/ton** *Potrošnja energije,* kWh/ton
1	small	69	79
2	small	69	79
3	large	138	100
4	large	138	100
5	large	138	100
6	large	138	100

Table 2 Sample identification codes
Tablica 2. Oznake uzoraka

Code / *Oznaka*	**Sample** / *Uzorak*
Ctrl	Control / *kontrolni*
Pre	Mechanical pre-treatment by refiner *mehanički predtretman rafiniranjem*
1 up to 6	Microfluidizer passes 1 up to 6 *prolazak kroz mikrofluidizator od 1 do 6 puta*

The films with the base weight of 30 g/m^2 were conditioned in a standardized environment at 22 °C and 50 % relative humidity for 24 hours.

2.2.6 Nanofilm testing
2.2.6. Ispitivanje nanofilmova

The characterization of NFLC films were carried out according to the following standards: density (ISO 534), thickness (Tappi 411 om 97), roughness (Tappi 538 om 01), tensile strength (ISO 1924-2), burst strength (TAPPI 403om 02), opacity and transparency (ISO 2471). The selected NFLC films were further analyzed by field emission scanning electron microscopy (FE-SEM; FEI Company). The fiber diameter of NFLC films from soda and MEA pulps was measured by image-J software and the average dimension of 100 fibers was reported.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Chemical composition of wheat straw
3.1. Kemijski sastav pšenične slame

The typical distribution of cellulose, hemicellulose, lignin, and extractives for softwood is 42 %, 27 %, 28 %, and 3 %, respectively, while hardwood distribution is 45 %, 30 %, 20 %, and 5 %, respectively (Smook, 2002). Table 3 presents the results of the chemical composition of wheat straw. Compared to softwoods and hardwoods, wheat straw has higher content of cellulose and lower content of lignin, and these properties can be positive in regard to energy and chemical consumption as well as production yield of pulping processes. However, higher ash content can cause some difficulties in recovery of black liquors in wheat straw based pulp and paper mills.

Table 3 Chemical composition of wheat straw
Tablica 3. Kemijski sastav pšenične slame

Component / *Komponenta*	**Value** / *Vrijednost,* %
Cellulose / *celuloza*	49.78
Lignin / *lignin*	19.64
Hemicelluloses / *hemiceluloza*	20.37
Extractives soluble in alcohol - acetone / *ekstraktivi topljivi u alkohol-acetonu*	4.93
Ash content *sadržaj pepela*	5.28

3.2 Pulp properties
3.2. Svojstva pulpe

Table 4 shows the properties of soda and MEA pulps. As it can be seen, MEA pulp has higher overall yield (60 %) than soda pulp (48 %). One of the remarkable properties of MEA is the conservation of hemicelluloses of the lignocellulosic materials in the pulping process that results in higher pulp yield (Hedjazi *et al.,* 2009; Hedjazi *et al.,* 2011). MEA process resulted also in pulps with lower kappa number than that of soda process. In this study, we have tried to keep the kappa numbers of soda and MEA pulps the same as much as possible to have better comparison of refining effect on

Table 4 Soda and MEA pulp properties
Tablica 4. Svojstva natronske i MEA pulpe

Pulping *Priprema pulpe*	**Properties** / *Svojstva*									
	Screen pulp yield, % *Prinos prosija-vanja, %*	**Screen reject, %** *Otpad prosija-vanja, %*	**Total pulp yield, %** *Ukupan prinos vlakana, %*	**Kappa no.** *Kappa-broj*	**ISO Brightness, %** *ISO svjetlina, %*	**Visco-sity ml/g** *Viskoz-nost, ml/g*	**Beating degree, SR** *Stupanj mljevenja,* SR	**Extractive, %** *Ekstraktivi, %*	SiO_2, %	**Ash, %** *Pepeo, %*
Soda	43	5	48	18	24.1	805	21	0.5	0.54	1.82
MEA	57.2	2.8	60	16.5	36.3	915	30	1.45	1	2.95

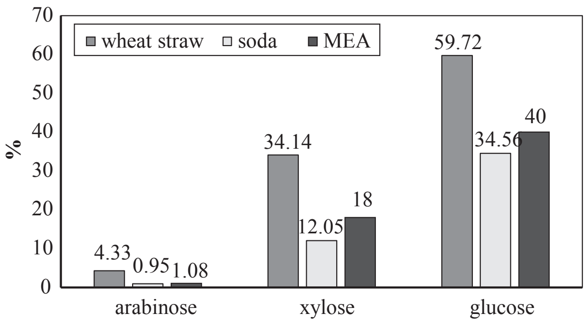

Figure 1 Monosaccharaides composition of wheat straw, soda and MEA pulps
Slika 1. Sastav monosaharida od pšenične slame te od natronske i MEA pulpe

the pulps. The higher beating degree of MEA pulp is attributed to its higher hemicelluloses content, which in turn facilitates the refining process and thus reduces the energy consumption in refiner to achieve certain freeness or beating degree.

As figure 1 shows, MEA pulp had higher xylose and glucose contents than soda pulp. This means that the carbohydrates are protected better in MEA pulping. The mechanism of conservation of carbohydrates by MEA was not completely known and there are contradictory theories regarding this matter. Some researchers believe MEA acts as a reducing agent and with converting the reducing ends of cellulose chains to alditols stops the peeling reaction. Some others have reported that monoethanolamine stabilizes polysaccharides by condensation reaction of aldehyde and formation of imines. Based on this theory, the stability of carbohydrates is due to radical reduction in presence of MEA ((Hedjazi *et al.,* 2009; Hedjazi *et al.,* 2011; Salehi *et al.,* 2014; Ghahremani *et al.,* 2014).

3.3 Physical properties of NFLC films
3.3. Fizička svojstva NFLC filmova

Table 5 presents the physical properties of soda and MEA pulps and nanofilms including film thickness, density and roughness. An increase in energy consumption, caused by production of smaller nanofibers with higher compressibility, resulted in sheet texture with less thickness and roughness as well as higher density. Soda pulps and nanofilms had higher calliper and lower roughness compared to those prepared with MEA.

3.4 Mechanical properties of NFLC films
3.4. Mehanička svojstva NFLC filmova

Figure 2 shows the results of tensile indices of sheets produced with soda and MEA pulps (Ctrl) and those of mechanically pre-treated ones (Pre) together with the tensile index of nanofilms prepared from NFLC passed through microfluidizer up to six times (1 up to 6). As shown in Fig. 4, sheets prepared with control samples had the lowest tensile index of 34 and 37 N·m/g for soda and MEA pulps, respectively (47 % and 43 %). When a mechanical pre-treatment was applied, the tensile index significantly increased. In the case of NFLC nanopapers, the increase in number of passes resulted in increased energy consumption and significant improvement of tensile index. The maximum tensile index was observed after the third pass through microfluidizer for NFLC film prepared with soda and MEA (113.5 and 119.86 Nm/g, respectively). Energy consumption by microfluidizer for the current passage was 258 kwh/t. The present results showed the high efficiency of MEA in terms of saving energy to reach the highest tensile index. The tensile strength of nanofilms showed the level or power of hydrogen bonding formed between nanofibers in paper network (Ahmadi *et al*., 2018). The tensile strength of nanofilms showed the level or power of hydrogen bonding formed between nanofibers in paper network. The tensile strength of nanofilms increased with the increase of bonding number or strength. This strength is also dependent on bonding number on one side and individual nanofibers strength on the other. In general, increasing the fibrillation induced by addition of energy consumption in microfluidizer (increased number of passes) as well as applying pre-treatment resulted in an increased tensile strength. Increase in the number of passes (over 3 passes) only caused the increase of energy consumption without effect on improving the tensile index so fiber damage caused the decrease of the tensile index. Other researchers have reported the same trend in production of NFCs by microfluidizer (Spence *et al.,* 2011; Ahmadi *et al*., 2018).

Table 5 Physical properties of pulp sheets and NFLC films from soda & MEA pulping
Tablica 5. Fizička svojstva listova pulpe i NFLC filmova dobivenih od natronske i MEA pulpe

Pulping process *Proces dobivanja pulpe*	**Properties** *Svojstva*	**Ctrl**	**Pre**	**Microfluidizer pass number** *Broj prolaska kroz mikrofluidizator*					
				1	**2**	**3**	**4**	**5**	**6**
Soda	Thickness / *debljina,* µm	53^{e}	49.4^{d}	44^{c}	41.4^{b}	41^{b}	37.2^{b}	36^{b}	29.8^{a}
	Density / *gustoća,* g/cm^3	0.49^{f}	0.51^{e}	0.65^{d}	0.66^{d}	0.78^{c}	0.76^{b}	0.79^{a}	0.81^{a}
	Roughness / *hrapavost,* ml/min	3410^{f}	3228^{e}	2636^{d}	2598^{c}	2476^{c}	2263^{b}	2182^{b}	1974^{a}
MEA	Thickness / *debljina,* µm	51^{f}	46.2^{e}	37.2^{d}	36.2^{d}	33.8^{c}	32^{b}	28.8^{a}	28.7^{a}
	Density / *gustoća,* g/cm^3	0.51^{g}	0.53^{f}	0.63^{e}	0.66^{d}	0.73^{c}	0.77^{b}	0.78^{b}	0.84^{a}
	Roughness / *hrapavost,* ml/min	3230^{e}	3120^{e}	3037^{de}	2863^{d}	2664^{c}	2284^{b}	2270^{b}	2027^{a}

*Lower case letters on the bars (a-f) show Duncan multiple range grouping of means. / *Mala slova (a – f) označuju grupiranje srednjih vrijednosti prema Duncanovu višestrukom rasponu.*

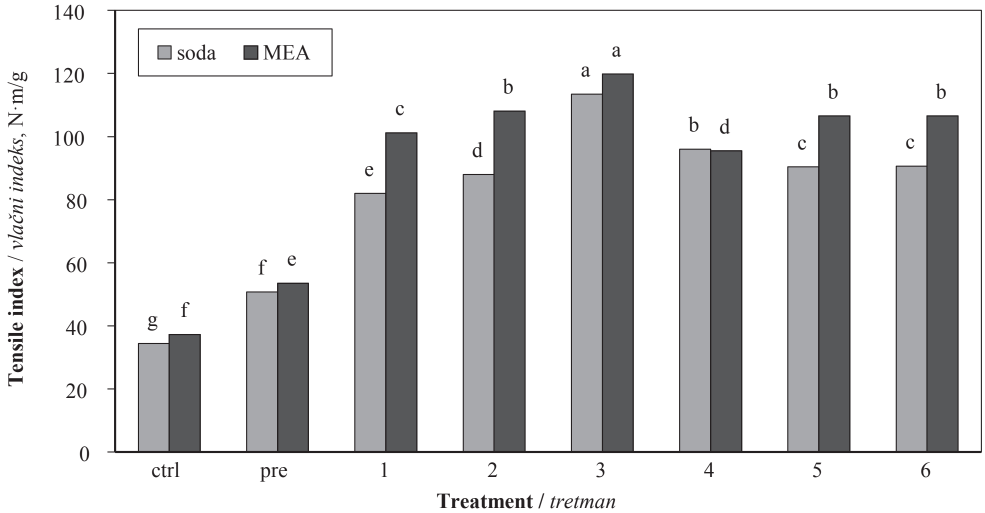

Figure 2 Tensile index of pulp sheets and NFLC films from soda and MEA pulping
(Lower case letters on the bars show Duncan multiple range grouping of means)
Slika 2. Vlačni indeks ploča pulpe i NFLC filmova dobivenih od natronske i MEA pulpe
(mala slova označuju grupiranje srednjih vrijednosti prema Duncanovu višestrukom rasponu)

Figure 3 shows the burst index of sheets made from Ctrl and Pre soda and MEA pulps together with the burst indices of nanofilms prepared with NFLC passed through microfluidizer up to six times. Burst index of NFLC films from soda and MEA pulping increased with the addition of energy consumption in microfluidizer, and the maximum value of 8.5 kP·m^2/g and energy consumption of 458 kwh/t were obtained after five passes through microfluidizer. Also, burst indices increased by 500 % and 466 %, for soda and MEA prepared nanofilms, respectively, at given total energy consumption of 628 kwh/t (refiner and 5 passes through microfluidizer). Burst index of sheets significantly increased with the increase of energy consumption due to the increase in fiber flexibility and the formation of more hydrogen bonds between fibers.

3.5 Optical properties of NFLC films
3.5. Optička svojstva NFLC filmova

Figures 4 and 5 depict opacity and transparency of pulp sheet produced with soda and MEA pulps (control samples) and those of mechanically pre-treated ones together with the opacity and transparency of nanofilms prepared with NFLC passed through microfluidizer up to six times. Soda and MEA control samples had higher opacity and lower transparency values. With the increase of the number of passes through microfluidizer, the opacity values of NFLC films decreased, but their transparency values increased. Generally, nanofilm opacity decreases with increasing the number of linkages between nanofibers along with denser NFLC texture. Thus, the opacity of nanofilms increased with increasing the fibrillation by chemical

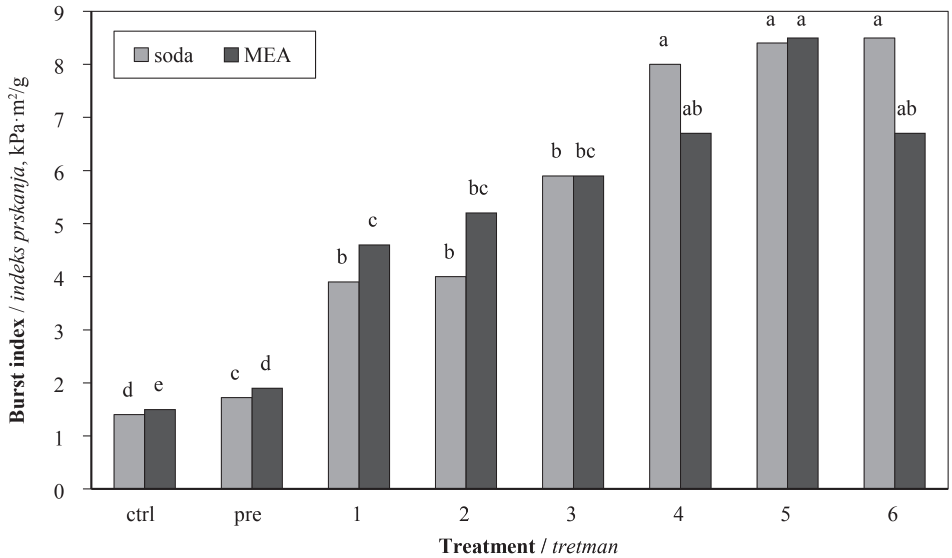

Figure 3 Burst index of pulp sheets and NFLC films from soda and MEA pulping
(Lower case letters on the bars show Duncan multiple range grouping of means)
Slika 3. Indeks prskanja ploča pulpe i NFLC filmova dobivenih od natronske i MEA pulpe
(mala slova označuju grupiranje srednjih vrijednosti prema Duncanovu višestrukom rasponu)

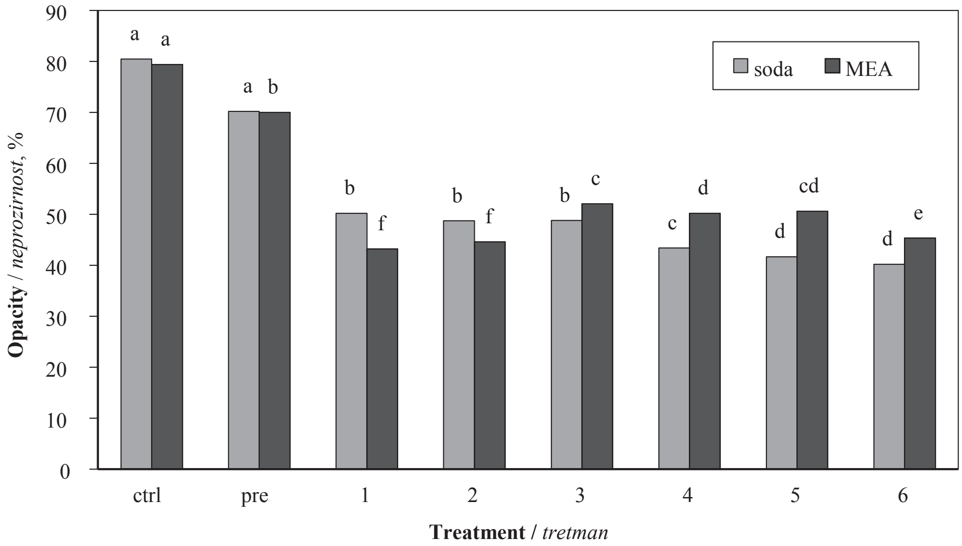

Figure 4 Opacity of pulp sheets and NFLC films from soda and MEA pulping
(Lower case letters on the bars show Duncan multiple range grouping of means)
Slika 4. Neprozirnost ploča pulpe i NFLC filmova dobivenih od natronske i MEA pulpe
(mala slova označuju grupiranje srednjih vrijednosti prema Duncanovu višestrukom rasponu)

or mechanical pre-treatments. In this case, the highest opacity was recorded in the control sample (around 80 %). The opacity of sheets decreased after refining pre-treatment due to fiber shortening, which decreases light scattering. The loss in opacity is continued because of the presence of fibers in nano scales. (Hassan *et al.,* 2011; Ankerfors, 2012; Ahmadi *et al*., 2018).

Among the nanofilms made from soda and MEA NFLC under different energy consumption, the highest transparency was obtained as 76.11 and 72.48 %, respectively. Total energy consumption was 728 kWh/t for soda NFLC and 628 kWh/t for MEA NFLC. In general, the transparency of samples increased after mechanical pre-treatment compared to the control one. Also, there was an increase in the transparency of samples after fibrillation by microfluidizer. Pre-treatment and nanofibrillation caused to change the fiber dimensions from micro scale to nano scale. As the dimension of nanoparticles is lower versus UV-visible wavelength (200-1000 nm), there is no obstacle for the increase of light transmittance and consequently transparency values of samples. Transparency can also be increased when surface roughness decreases (Nishino *et al.,* 2005; Yousefi *et al.,* 2011).

3.6 FE-SEM analysis
3.6. FE-SEM analiza

Figure 6 shows the FE-SEM micrographs of soda pulp sheet (a), MEA pulp sheet (b), soda-NFLC films (c) and MEA-NFLC films (d). The surface of papers from pre-treated fibers was non-uniform with somewhat intact fibers and a large density of inter-fiber

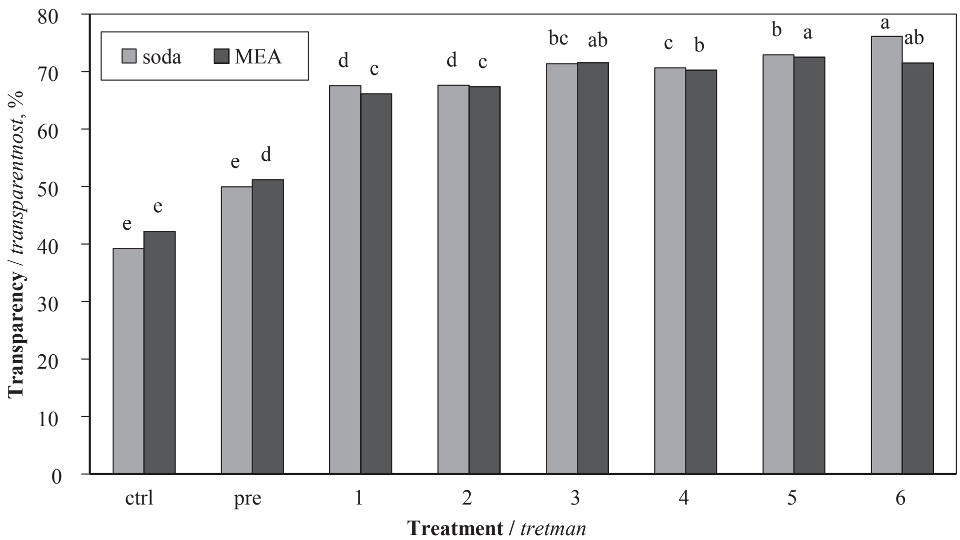

Figure 5 Transparency of pulp sheets and NFLC films from soda and MEA pulping
(Lower case letters on the bars show Duncan multiple range grouping of means)
Slika 5. Transparentnost ploča pulpe i NFLC filmova dobivenih od natronske i MEA pulpe
(mala slova označuju grupiranje srednjih vrijednosti prema Duncanovu višestrukom rasponu)

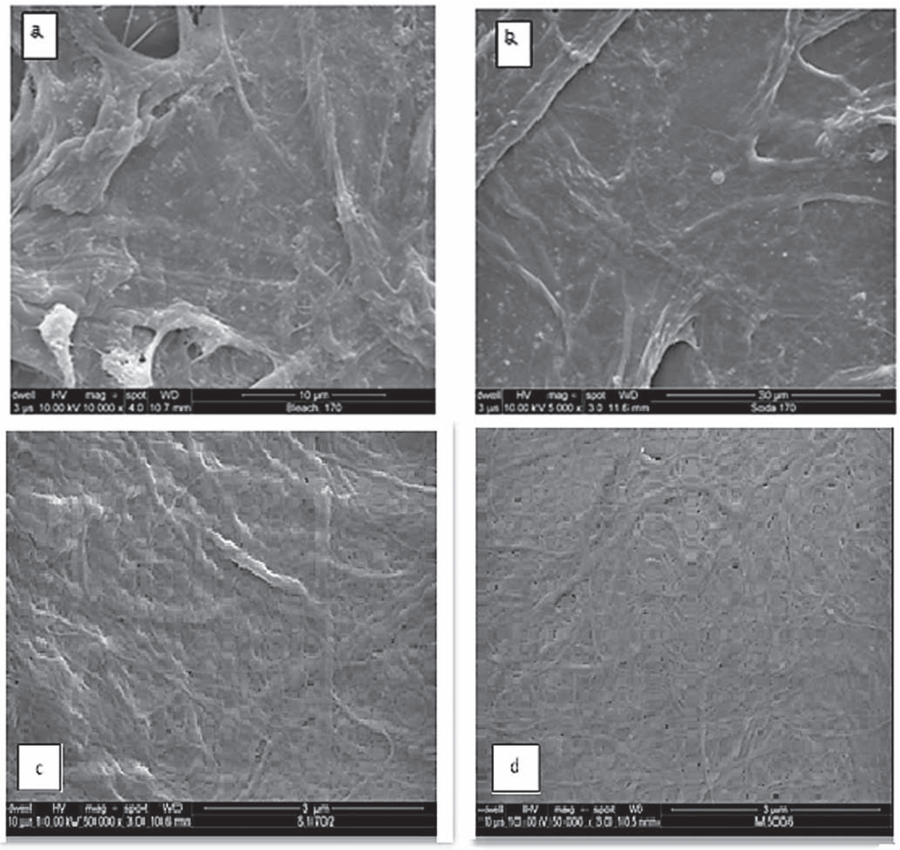

Figure 6 FE-SEM micrographs of a) soda pulp sheet, b) MEA pulp sheet, c) soda-NFLC films and d) MEA-NFLC films
Slika 6. FE-SEM mikrografije: a) listovi natronske pulpe, b) listovi MEA pulpe, c) soda-NFLC filmovi, d) MEA-NFLC filmovi

pores. However, after the sample was passed through microfluidizer, the NFLC films displayed a more uniform surface structure, smaller fibrils and fibril bundles.

Figure 7 depicts the average diameter for 100 fibers of each sample. The average diameter of soda and MEA control samples obtained was 18500 and 19100 nm, respectively. By refining pre-treatment, the corresponding values reached 12000 and 14000 nm, respectively. After downsizing with 2 passes (158 kWh/t) thorough microfluidizer, the corresponding values dramatically decreased to 52 and 45 nm, respectively. Also, the corresponding diameter values decreased to 38 and 36 nm, respectively, after 6 passes (558 kWh/t).

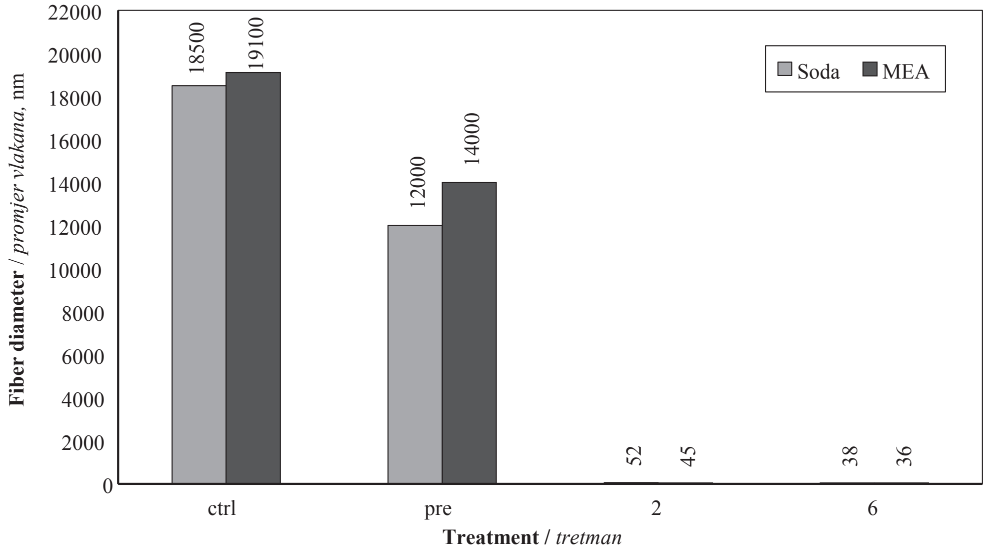

Figure 7 Fibers diameter of NFLC films from soda and MEA pulps
Slika 7. Promjer vlakana NFLC filmova dobivenih od natronske i MEA pulpe

Based on these results, it can be concluded that the average diameters of fibers decreased with the increase of energy consumption. Also, the average diameter of soda-NFLC and MEA-NFLC decreased 486 and 530 fold compared to the average diameters of corresponding control samples.

4 CONCLUSIONS
4. ZAKLJUČAK

In this study, two different processes using MEA and soda were used to produce unbleached pulp from wheat straw. The unbleached pulps were then downsized using microfluidizer with different passes and energy consumptions. The results showed that the production of NFLC from pulp obtained by MEA method leads to better properties with less energy consumption compared to the soda pulp production method. MEA pulping led to higher yield than soda pulping at given delignification rate. Also, MEA pulping had more refine-ability versus soda pulping, so that the cellulosic nanofibers with higher strength properties might be produced by microfluidizer of wheat straw with lower energy consumption versus soda pulping process. The results showed that using energy led to improve the strength properties of lignocellulosic nanofibers to some extent, while overuse of energy had no positive effect on improving these properties and only caused to increase the production costs. It was concluded that the MEA pulping process was more efficient than the soda pulping process in similar energy consumption.

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