**Improved chemical reactivity of lignocellulose from high solids content defibrillation by twin-screw extrusion**

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ABSTRACT

The low reactivity of lignocellulose limits the effective chemical conversion of lignocellulose biomass into functional bioproducts. Conventional wet micro-fibrillation using a grinder or homogenizer can improve the chemical accessibility of lignocellulose but has limited productivity for industry by the low processing solids content. The presented work demonstrates fibrillation of lignocellulose at high solids content up to 70 wt% can be achieved by a pilot-scale twin-screw extruder. Morphological characterizations of the extruded lignocellulose show that twin-screw extrusion can effectively fibrillate the wood pulp into submicron fibrils, and the degree of fibrillation is enhanced by operating at higher solids content, making for an economical process. The treated wood pulp presents 2.08 and 4.8 times higher water retention capacity and specific surface area, respectively, as compared with the original material, thus opening the cell wall structure for improving chemical accessibility. Acetylation results show that twin-screw extrusion pre-treatment can significantly accelerate the chemical modifications of lignocellulose by 50% and reduce chemicals usage. This method for micro-fibrillating lignocellulose shows high reported consistency and should be of great interest to the bioplastics industry.

**Key words:** Lignocellulose; twin-screw extrusion; micro-fibrillation; chemical reactivity

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## 1. Introduction

In recent decades, many stakeholders of the plastics industry have shown interest in building manufacturing capacity for bioplastics from the renewable sources to reduce their reliance on petroleum and get ahead of looming regulatory restrictions. Some bioplastics, *e.g.* polylactic acid, featuring varying levels of biodegradability have found commercial success, but have questionable futures being produced from food-based resources including corn and plant oils. As compared with food-based biomass, lignocellulose, which is the main constituent of woody plants, grasses, and crops, has more abundant availability and feasible renewability without sacrificing food security, and thus is considered as a promising alternative for food-based biomass in bioplastics production (Brodin et al., 2017; Isikgor and Becer, 2015; Ten and Vermerris, 2013). But isolated native lignocellulose shows low chemical accessibility to its complex assembly of hemicellulose, cellulose, and lignin components on account of strong inter-and intra-molecular hydrogen bonding. Lignocellulose is insoluble in common organic solvents and incapable of flow like commodity thermoplastics, which necessitates its functional modification whether by chemical or bio-fermentation methods to prepare bioplastics. Both approaches require vigorous reaction conditions and long reaction time (Bao et al., 2018; J. Chen et al., 2017; M. J. Chen et al., 2017; Tian et al., 2018; Zhen et al., 2016).

It is well recognized that mechanical treatment is an effective technique which can significantly improve the chemical accessibility of lignocellulose in bioconversion processes, *e.g.* mechanical milling of Douglas-fir wood at different moisture contents can give a 2-6 fold increase in its enzymatical digestibility (Lee et al., 2010). The possible mechanism by which mechanical treatment alters the chemical accessibility of

lignocellulose includes (*i*) increasing the external surface area of lignocellulose by size reduction, (*ii*) creation of more pores and voids in lignocellulose, and (*iii*) increasing the internal surface area due to fibers defibrillation (Duque et al., 2017; Lee et al., 2009). In recent years, twin-screw extrusion has been considered as the most promising practice for continuous industrial processing of agricultural and forestry feedstocks (Kratky and Jirout, 2011; Kumar and Sharma, 2017; Zheng and Rehmann, 2014). As compared with other commonly used mechanical treatment methods including ball milling, beating, and homogenization, twin-screw extrusion has the capacity to operate at higher solid loadings as well as lower energy consumption (Baati et al., 2017; Chen et al., 2013; Ho et al., 2015; Rol et al., 2017). Several research efforts have been made on utilizing twin-screw extrusion in the pre-treatment of varied lignocellulose sources including crops straw (Choi et al., 2013; Choi and Oh, 2012; Um et al., 2013), bagasse (da Silva et al., 2013; Vandenbossche et al., 2016), and hardwood pulp (Liu et al., 2016) for the purpose of maximizing yields of fermentable sugars in secondary operations. However, there have been no reports on twin-screw extrusion pre-treatment of lignocellulose for consideration of subsequent heterogeneous chemical modifications of lignocellulose which is an important route to prepare bioplastics from biomass.

Of particular concern is whether the pre-treatment can be done without the additives used for micro-fibrillation in enzymatic hydrolysis processes. The reported additives for twin-screw extrusion of lignocellulose include glycerol (Zhang et al., 2017), ionic liquids (da Silva et al., 2013), and dilute acids or alkalines (Cha et al., 2016; Kim et al., 2013; Liu et al., 2013; Senturk-Ozer et al., 2011). However, these additives in the extruded lignocellulose have to be subsequently removed so not to inhibit the subsequent enzyme reaction, which

would be similarly needed for most chemical modifications as well. The cleaning step has been reported on occasions to recover previously lost hydrogen bonding associations, *e.g.* dried powder from the dehydration of aqueous suspensions of cellulose nanofibers has shown poor re-dispersity in water (Velásquez-Cock et al., 2018). In addition, these liquid additives usually cause severe degradation of the lignocellulose during micro-fibrillation, which is desired for enzyme hydrolysis but may not be accepted for chemical modifications intended to prepare a bioplastic. As compared with the enzymatical hydrolysis, chemical modifications of lignocellulose typically require higher solids loading, shorter reaction times and better heat and mass transport efficiency, which matters particularly if one eventually attempts to combine pre-treatment and modification in the same production process. Hence, it is also vital to know the relationship between the reactivity of lignocellulose in chemical modifications and its physical properties as a result of extrusion pre-treatment.

The present study examines twin-screw extrusion as a mechanical treatment for micro-fibrillation of lignocellulose, reporting on physical properties of the fibers and investigates whether the extruded product exhibits suitable reactivity for chemical modification in the absence of commonly used additives mentioned above. The goal was to demonstrate an approach that is effective for de-structuring wood pulp at high solids content with minimal degradation.

## 2. Experimental section

### *2.1. Materials*

Never-dried aspen high yield wood pulp was received from Tembec (Montreal, Quebec) and used throughout this study as a model lignocellulose. The initial moisture content of the pulp was 8.4 wt% determined by a moisture analyzer (HG63, Mettler Toledo, USA) at 105 ºC setpoint temperature. The acid insoluble lignin content of the pulp was 8.16 wt% determined by the TAPPI-T method 222 om-02. Congo red and (analytical grade) was purchased from Sigma-Aldrich, Canada. Sodium phosphate, dibasic and sodium phosphate, monobasic both in ACS grade were bought from Fisher Scientific, Canada.

### *2.2. Extrusion pre-treatment of mechanical pulp*

A ZSE-HP 27 mm 40 L/D co-rotating intermeshing twin-screw extruder (American Leistritz Extrusion Corp.; Somerville, NJ) was used to mechanically micro-fibrillate the wood pulp. As shown in Fig. 1, the screw configuration was composed of conveying screws elements and 90 º offset kneading elements to generate high shear stresses. Desired amounts of distilled water were pre-mixed with the pulp to prepare extrusion feedstocks with solids content at 20, 30, 40, 50, 60 and 70 wt%, respectively. The pre-wetting wood pulp was manually fed into the extruder at ~2.5 kg/h. The temperature inside the extruder barrel was maintained close to 10 ºC by chilled water, and the rotating speed of screws was set at 250 rpm. Each extrusion feedstock having a certain solids content was extruded for 1, 3, 5 and 7 passes. Repeated passes were used in place of modifying the screw design to determine the number of shear events appropriate to fibrillate the pulp. Samples were collected from the exit die of the extruder and referenced in the results based on a naming

nomenclature of SP*x-y*, where *x, y* represented the solids content and number of passes through the extruder, respectively.

*2.3. Characterizations of extruded mechanical pulp*

*2.3.1. Solid content changes*

The extruded mechanical pulp was collected and sealed in plastic bags. The final solids content of these samples was determined using a moisture analyzer (HG63, Mettler Toledo, USA) set for isothermal heating at 105 ºC.

*2.3.2. Water Retention Values*

Water retention values *(WRV)* were measured by a modified TAPPI method UM 256. Briefly, 1 g of the extrusion treated mechanical pulp was dispersed in 40 mL water and boiled for 30 min. Then the suspension was centrifuged in a tube with an inserted cellulose acetate membrane filter at 9000 g for 30 mins. Obtained wet samples were weighed and dried in an oven at 105 ºC for 2 h. The WRV was then calculated by using the following equation:

$$\text{WRV}\ (\%) = \frac{W_1 - W_2}{W_2} \qquad (1)$$

where $W_1$ and $W_2$ are the weights of wet and dried samples, respectively

*2.3.3. Specific Surface Area*

Specific surface area of the extruded mechanical pulp was evaluated by Congo red dye adsorption experiments (Samiey and Dargahi, 2010; Spence et al., 2010). In brief, an extrusion treated mechanical pulp sample with a 0.05 g dry weight was dispersed in 20 mL phosphate buffer to form the suspension with a pH of 6. The suspension was then treated with varying amounts (5-25% of the weight of the pulp) of Congo red and incubated in a

shaking water bath at 60 °C for 24 h. The sample was finally centrifuged at 16500 g for 15 min, and the concentration of Congo red in the supernatant was determined by UV–Vis absorption (DU 800, Beckman Coulter, USA) at 500 nm. The maximum adsorbed amount of Congo red $A_{max}$ in mg/g by the pulp was calculated using Langmuir isotherms:

$$\frac{[E]}{[A]} = \frac{1}{K_{ad} A_{max}} + \frac{[E]}{A_{max}} \quad (2)$$

where *[E]* is the solution concentration of Congo red at adsorption equilibrium in mg/ml, *[A]* is the equilibrium adsorbed amount of Congo red on the mechanical pulp surface in mg/g, and $K_{ad}$ is the Langmuir adsorption equilibrium constant. The specific surface area (SSA) of the extruded mechanical pulp was finally calculated by equation (3):

$$SSA = \frac{A_{max} \times N \times SA}{MW \times 100} \quad (3)$$

where *N* is Avogadro's constant, *SA* is the surface area of a single dye molecule (1.73 $nm^2$), and *MW* is the molar mass of Congo red (696 g/mol).

*2.3.4. Light Microscope*

25 µL of a 0.05 wt% extruded mechanical pulp suspension was dropped on a pre-cleaned glass slide. A coverslip was put on the liquid samples immediately after dropping to minimize aggregation of the pulp fibres. The samples were air dried for 24 h, and then observed and imaged by an imaging Microscope (Axioplan 2, Carl Zeiss, German).

*2.3.5. Scanning Electron Microscopy*

Samples of the extruded mechanical pulp were diluted to approximately 0.1% and vacuum filtered through a 1 µm nucleopore track-etch membrane while washing with excess water. A filtered sample was air dried and mounted on an SEM stub before being sputter coated

with 6 nm Pt/Pd. Images were captured using an SU8000 FE-SEM (Hitachi, Japan) operating at 5 KV.

*2.3.6. Sedimentation testing*

Extruded mechanical pulp was dispersed into deionized water to obtain a 7 mL aqueous suspension with solids content of 1 wt% in a glass vial. The vial was sealed and shaken while inverted for 2 h before being left for stabilization. Pictures were taken after 2 days free-standing, and the heights of the total suspension ($H_o$) and the sediment ($H_s$) were measured by ImageJ image analysis software (National Institutes of Health, USA). The sedimentation ratio is the sediment height relative to the total surface liquid height ($H_s/H_o$).

*2.4. Solvent free acetylation of the pre-treated mechanical pulp*

Extruded mechanical pulp was vacuum-dried at 90 ºC for 24 h prior to acetylation. For solvent-free acetylation of the mechanical pulp, 2 g dried extrusion pre-treated mechanical pulp was put into a 50-mL flask containing 12 mL acetic anhydride. 0.2 g anhydrous zinc chloride acting as a catalyst for the acetylation was pre-dissolved in the acetic anhydride by magnetic stirring for 5 mins at 80 ºC. The reaction took place at 120 ºC for 30 mins, and samples were taken out at times of 2, 4, 6, 8, 12, 16, 20, and 30 mins. The reaction was stopped by adding 10-fold water into the system. Each sample was filtered and repeatedly washed with 0.5 M sodium carbonate solution until its pH value reached ~7. Finally, the wet acetylated mechanical pulp was vacuum dried at 75 ºC for 24 h.

*2.5. Determination of the degree of substitution of acetylation the pulp*

Accurately weighed 0.1 g dried acetylated mechanical pulp was put into a 25-mL glass vials. 5 mL of 0.25 M NaOH and 5 mL anhydrous ethanol were added to the 0.1 g acetylated mechanical pulp. The mixture was left to free-standing for 24 h and then 10 mL

0.25 M HCl was added to the system. After 30 mins, the mixture was titrated using 0.25 M NaOH with phenolphthalein indicator. The acetyl group grafted on the mechanical pulp was calculated by equation (4):

$$\text{Acetyl content (wt\%)} = \frac{[(V_1 + V_2)C_1 - V_3C_2] \times 43}{m} \times 100\% \qquad (4)$$

where $V_1$ is the volume of NaOH added to the system before the titration, $V_2$ is the volume of NaOH consumed in the titration, $C_1$ is the NaOH concentration, $V_3$ is the volume of HCl added to the system before the titration, $C_2$ is the concentration of HCl, $m$ is the weight of the sample, and $43$ is the molecular weight of an acetyl group.

## 3. Results and discussions

### *3.1. Solids content changes during twin-screw extrusion*

Solids content played a significant role during the process on the morphology of the final products. It was vital to know the true solids content of the pulps during extrusion processing, especially at high numbers of extrusion passes. As shown in Table 1, the solids content of all pre-wetting mechanical pulps had increased very little after five passes through the extruder but after seven passes, a significant increase in solids content was reported. For the seventh pass, sample $SP_{70}$-$_7$ showed the highest moisture loss of ~8.25% compared to its original setpoint. Multiple passes in an industrial process may not be practical but we believe a longer extruder or tandem extrusion setup would accomplish the same results as our multi-pass laboratory configuration. The loss of moisture from the pulp substrates was attributed to heat generated from the friction between pulp fibers, though it was a bit surprising that it took seven passes for the effect to be noticeable. Hence, a solids

content ~60 wt% can be considered as the maximum solids content which can be used for effective defibrillation of mechanical pulp lignocellulose by twin-screw extrusion.

### *3.2. Influence of twin-screw extrusion on the morphological properties of lignocellulose*

#### *3.2.1. Defibrillation and size reduction*

WRV quantifies the water absorption capacity of lignocellulose fibrils and has been proven to be a reliable indicator for the extent of micro- and nano-fibrillation of pulps (Qin et al., 2016). As shown in Fig. 2, the WRV of twin-screw extruded mechanical pulps were all higher than that of the original raw material, indicating greater water absorption was achieved by the wet twin-screw extrusion. With up to three extrusion passes, the WRV of the extrusion treated pulp increased consistently with increasing solids content, suggesting beneficial fibers disintegration at higher solids content. For a greater number of extrusion passes exceeded three times, the WRV showed a drop as the solids content exceeded 50 wt% even though at lower solids values the WRV continued to show even greater improvement. Sample $SP_{60\text{-}5}$ presented the maximum WRV of 215.73% which was 2.08 times higher than that of the raw material.

Photographs of the collected samples reflected fiber characteristics that corresponded with the noted trend for WRV of twin-screw extrusion treated mechanical pulps. As shown in Fig. 3, the pulp chips of the raw material had been pulverized into smaller sized granules or fine powder after 5 passes through the twin-screw extruder depending on the water content. Sample $SP_{60\text{-}5}$ (Fig. 3c) was process into fine powder, showing more apparent surface area as would be expected based on its WRV than sample $SP_{30\text{-}5}$ (Fig. 3b) which appeared in the form of granules. But for the sample $SP_{70\text{-}5}$ (Fig. 3d) with an initial 70 wt% solid content, hornification was observed with an obvious number of flakes appearing in the collected

powder. A similar phenomenon was observed for sample $SP_{70\text{-}7}$ (not shown), which may be the reason why the WRV started to decline by the 5$^{th}$ pass at 70 wt% solids content. Although a slight drop in WRV was also observed for sample $SP_{60\text{-}7}$, no hornification was found in its collected powder.

Light microscopy was employed to further investigate the morphological changes of mechanical pulps after twin-screw extrusion treatments with images shown in Fig. 4. Fig. 4b shows that fiber length reduction was the main effect of multiple extrusion passes on the mechanical pulp at a low solids content of 30 wt%. The average fiber length observed of sample $SP_{30\text{-}5}$ was ~300 μm which was 41.7% of the length of the original pulp fibers. A small amount of microfibrils separated from the pulp substrate was also found in sample $SP_{30\text{-}5}$. Hence, the length reduction and defibrillation were both considered to be contributors to the increase in WRV at a low solids content (30 wt%). When the solids content was increased to 60 wt%, Fig. 4c shows that not only was the length of the mechanical pulp fibers significantly reduced, but that a much greater degree of defibrillation had occurred as well compared to sample $SP_{30\text{-}5}$. Most of the original pulp fibers were processed into hair-like microfibrils for sample $SP_{60\text{-}5}$. Micro-fibrillation appears to dominate as solids content increased, reflected by the higher WRV among the treated pulps. For more aggressive extrusion conditions, whether by an increase in the number of extrusion passes ($SP_{60\text{-}7}$) or solids content ($SP_{70\text{-}5}$ and $SP_{70\text{-}7}$), both would cause a visual aggregation of the extruded pulps to a certain extent, as displayed in Fig. 4d-f, which seems consistent with the fact that WRV dropped for these samples.

SEM images of the samples $SP_{60\text{-}5}$ and $SP_{70\text{-}7}$ (Fig. 5) gave more detailed information on their difference in microstructure. For sample $SP_{60\text{-}5}$, it was mainly consisted of individual

microfibrils with the width ranging from 5-30 μm, whereas sample $SP_{70\text{-}7}$ mainly contained short micro-sized fragments. It was believed that the highest shear damage was generated during the extrusion of $SP_{70\text{-}7}$ because it had the least amount of water working as a lubricant in the system. Additionally, the insufficient amount of water during extrusion of $SP_{70\text{-}7}$ limited defibrillation of the pulp fibers due to poor swelling of the raw material. Hence, the extrusion of the mechanical pulp at 70 wt% solid content was mainly in the form of cutting fibers and detaching fibrils from the surface of the pulps. A similar result was also found by (Kekäläinen et al., 2014) in the high-pressure homogenization of TEMPO oxidized and bleached hardwood fibers, where hornified samples prepared by drying were cut into shorter fibers and fragments while the never-dried fibers without hornification were disintegrated directly into microfibrils.

Size reduction and defibrillation of mechanical pulps by twin-screw extrusion was further noted by sedimentation testing of the extruded pulps. Fig. 6 a-b displayed the observable sedimentation behavior of all collected mechanical pulps treated at different solids content after five passes through the extruder. After 4 hours of free standing, the water-rich phase at the top of all suspensions was still turbid, indicating that a considerable amount of fine fibrils were produced by the twin-screw extrusion. After 24 hours of free standing, it was found that this water-rich upper region in the vial for sample $SP_{20\text{-}5}$ had become totally clear without visible pulp fibers, whereas the upper regions in the vials for samples $SP_{40\text{-}5}$, $SP_{50\text{-}5}$ and $SP_{60\text{-}5}$ were still cloudy; high solids content appeared beneficial for the generation of microfibrils from the pulp substrate. This phenomenon was quantifiably displayed by the sedimentation ratio after 24 hours, which is given for all extrusion passes in Fig. 6c. Higher solids content was consistently correlated to a lower height of sediment,

which can also be interpreted as higher bulk density. A major reason for this relationship was that shorter fibers were produced at higher solid content extrusion, which more easily packed together densely. On the other hand, the defibrillated fine fibrils also increased the possible contact area between wood pulp, that's to say, increasing the van der Waals' attractive force between wood pulp fibers (Yano and Nakahara, 2004). The sedimentation ratios show deviation based on the number of extrusion runs for higher solids content than 50 wt%. The ratios show that samples, $SP_{60\text{-}7}$ and $SP_{70\text{-}7}$ exhibited a similar sedimentation nature as $SP_{60\text{-}1}$ and $SP_{70\text{-}1}$, which was due to the decrease in fine fibrils contents of $SP_{60\text{-}7}$ and $SP_{70\text{-}7}$ by aggregation.

*3.2.2. Improved specific surface area*

As shown in Fig. 7 of the specific surface areas of mechanical pulps, the mechanical pulps after twin-screw extrusion demonstrated higher specific surface areas than the original material. Passes 5 and 7 were compared in this analysis because notable changes in morphology of extruded wood pulps were observed, as shown in section 3.2.1. Generally, the results matched WRV with specific surface areas of the extrusion treated pulps increasing up to a solids content of 50 wt% but then decreased especially for samples $SP_{60\text{-}7}$, $SP_{70\text{-}7}$ and $SP_{70\text{-}5}$. Slightly different from the WRV, the specific surface areas did not significantly vary between these two passes through the extruder. The analysis indicated that mechanical pulp samples prepared in the twin-screw extruder up to 60 wt% solids content and after 5 passes can achieve the best fibrillation for chemical modification.

*3.3 Chemical accessibility related to morphological changes*

Acetylation is an effective reaction for the chemical modification of lignocellulose, and here it was used for the evaluation of chemical accessibility of the mechanically fibrillated

lignocellulose. As shown in Fig. 8 of the acetylation results of mechanical pulps, the extrusion pre-treatment not only increased the maximum content of acetyl groups that can be grafted on lignocellulose chains, but also had a noticeable effect on increasing the initial reaction rate. It was found a 96% of the maximum degree of substitution was quickly achieved for $SP_{60\text{-}5}$ after 12 mins, whereas the original raw material needed ~24 mins. This significant increase in initial reaction rate could reduce the feed concentration of the caustic anhydride species for the modification of lignocellulose. On the other hand, pre-treatment could allow chemical modification of lignocellulose to be carried out now in continuous reactors with short residence times, such as a twin-screw extruder, which would be beneficial for the industrialization of lignocellulose chemical conversion. $SP_{30\text{-}5}$ showed a slower initial reaction rate than sample $SP_{60\text{-}5}$, which was due to the weak defibrillation of wood pulp at low extrusion solid content. Correspondingly, $SP_{30\text{-}5}$ exhibited an increase in surface area by 225%, while a 360% increase for SP60-5 was more sufficient to make a notable impact on reactivity.

## 4. Conclusions:

This study demonstrates high solids content twin-screw extrusion is also sufficient to micro-fibrillate lignocellulose without aggressive chemical additives, with little apparent damage to lignocellulose chains under optimal conditions. At 60 wt% solids content and after 5 passes, mechanical pulp fibers are effectively processed into 7-30 μm wide hair-like microfibrils, which demonstrated improved water retention ability (216%) and surface area (18.85 $m^2/g$). More interestingly, the extruded wood pulp still has notably improved chemical reactivity after drying. This novel high solids content twin-screw extrusion supplies an economical and clean way for the industry to pre-treat lignocellulose biomass for further processing.

**Acknowledgements**

This research was funded under the "Clean Manufacturing and Nano-engineering of Sustainable Materials" Ontario Research Fund (ORF) grant (#07-41) led by Dr. Sain at the University of Toronto. The authors would like to extend their thanks to Sandra Gardner at Xerox Research Center of Canada for her technical help on SEM.

**References**

Baati, R., Magnin, A., Boufi, S., 2017. High Solid Content Production of Nanofibrillar Cellulose via Continuous Extrusion. ACS Sustain. Chem. Eng. 5, 2350–2359.

Bao, L., Zou, X., Chi, S., Dong, S., Lei, J., Wang, J., 2018. Advanced Sustainable Thermoplastics Based on Wood Residue Using Interface Nanomodification Technique 1800050, 1–12.

Brodin, M., Vallejos, M., Opedal, M.T., Area, M.C., Chinga-Carrasco, G., 2017. Lignocellulosics as sustainable resources for production of bioplastics – A review. J. Clean. Prod. 162, 646–664.

Cha, Y.L., Yang, J., Seo, S. Il, An, G.H., Moon, Y.H., You, G.D., Lee, J.E., Ahn, J.W., Lee, K.B., 2016. Alkaline twin-screw extrusion pretreatment of Miscanthus with recycled black liquor at the pilot scale. Fuel 164, 322–328.

Chen, J., Tang, C., Yue, Y., Qiao, W., Hong, J., Kitaoka, T., Yang, Z., 2017. Highly translucent all wood plastics via heterogeneous esterification in ionic liquid/dimethyl sulfoxide. Ind. Crops Prod. 108, 286–294.

Chen, M.J., Li, R.M., Zhang, X.Q., Feng, J., Feng, J., Liu, C.F., Shi, Q.S., 2017. Homogeneous Transesterification of Sugar Cane Bagasse toward Sustainable Plastics. ACS Sustain. Chem. Eng. 5, 360–366.

Chen, X., Kuhn, E., Wang, W., Park, S., Flanegan, K., Trass, O., Tenlep, L., Tao, L., Tucker, M., 2013. Comparison of different mechanical refining technologies on the enzymatic digestibility of low severity acid pretreated corn stover. Bioresour. Technol. 147, 401–408.

Choi, C.H., Kim, J.S., Oh, K.K., 2013. Evaluation the efficacy of extrusion pretreatment via enzymatic digestibility and simultaneous saccharification &fermentation with rapeseed straw. Biomass and Bioenergy.

Choi, C.H., Oh, K.K., 2012. Application of a continuous twin screw-driven process for dilute acid pretreatment of rape straw. Bioresour. Technol. 110, 349–354.

da Silva, A.S., Teixeira, R.S.S., Endo, T., Bon, E.P.S., Lee, S.-H., 2013. Continuous pretreatment of sugarcane bagasse at high loading in an ionic liquid using a twin-screw extruder. Green Chem. 15, 1991.

Duque, A., Manzanares, P., Ballesteros, M., 2017. Extrusion as a pretreatment for lignocellulosic biomass: Fundamentals and applications. Renew. Energy 114, 1427–1441.

Ho, T.T.T., Abe, K., Zimmermann, T., Yano, H., 2015. Nanofibrillation of pulp fibers by twin-screw extrusion. Cellulose 22, 421–433.

Isikgor, F.H., Becer, C.R., 2015. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. Polym. Chem. 6, 4497–4559.

Kekäläinen, K., Liimatainen, H., Illikainen, M., Maloney, T.C., Niinimäki, J., 2014. The role of hornification in the disintegration behaviour of TEMPO-oxidized bleached hardwood fibres in a high-shear homogenizer. Cellulose 21, 1163–1174.

Kim, T.H., Choi, C.H., Oh, K.K., 2013. Bioconversion of sawdust into ethanol using dilute sulfuric acid-assisted continuous twin screw-driven reactor pretreatment and fed-batch simultaneous saccharification and fermentation. Bioresour. Technol. 130, 306–313.

Kratky, L., Jirout, T., 2011. Biomass Size Reduction Machines for Enhancing Biogas Production. Chem. Eng. Technol. 34, 391–399.

Kumar, A.K., Sharma, S., 2017. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour. Bioprocess. 4, 7.

Lee, S.H., Teramoto, Y., Endo, T., 2010. Enhancement of enzymatic accessibility by fibrillation of woody biomass using batch-type kneader with twin-screw elements. Bioresour. Technol. 101, 769–774.

Lee, S.H., Teramoto, Y., Endo, T., 2009. Enzymatic saccharification of woody biomass micro/nanofibrillated by continuous extrusion process I - Effect of additives with cellulose affinity. Bioresour. Technol. 100, 275–279.

Liu, C., Van Der Heide, E., Wang, H., Li, B., Yu, G., Mu, X., 2013. Alkaline twin-screw extrusion pretreatment for fermentable sugar production. Biotechnol. Biofuels 6, 1–11.

Liu, W., Wang, B., Hou, Q., Chen, W., Wu, M., 2016. Effects of fibrillation on the wood fibers' enzymatic hydrolysis enhanced by mechanical refining. Bioresour. Technol. 206, 99–103.

Qin, Y., Qiu, X., Zhu, J.Y., 2016. Understanding Longitudinal Wood Fiber Ultra-structure for Producing Cellulose Nanofibrils Using Disk Milling with Diluted Acid Prehydrolysis. Sci. Rep. 6, 35602.

Rol, F., Karakashov, B., Nechyporchuk, O., Terrien, M., Meyer, V., Dufresne, A., Belgacem, M.N., Bras, J., 2017. Pilot-Scale Twin Screw Extrusion and Chemical Pretreatment as an Energy-Efficient Method for the Production of Nanofibrillated Cellulose at High Solid Content. ACS Sustain. Chem. Eng. 5, 6524–6531.

Samiey, B., Dargahi, M.R., 2010. Kinetics and thermodynamics of adsorption of congo red on cellulose. Cent. Eur. J. Chem. 8, 906–912.

Senturk-Ozer, S., Gevgilili, H., Kalyon, D.M., 2011. Biomass pretreatment strategies via

control of rheological behavior of biomass suspensions and reactive twin screw extrusion processing. Bioresour. Technol. 102, 9068–9075.

Spence, K.L., Venditti, R.A., Rojas, O.J., Habibi, Y., Pawlak, J.J., 2010. The effect of chemical composition on microfibrillar cellulose films from wood pulps: Water interactions and physical properties for packaging applications. Cellulose 17, 835–848.

Ten, E., Vermerris, W., 2013. Functionalized polymers from lignocellulosic biomass: State of the art. Polymers (Basel). 5, 600–642.

Tian, S.Q., Zhao, R.Y., Chen, Z.C., 2018. Review of the pretreatment and bioconversion of lignocellulosic biomass from wheat straw materials. Renew. Sustain. Energy Rev. 91, 483–489.

Um, B.H., Choi, C.H., Oh, K.K., 2013. Chemicals effect on the enzymatic digestibility of rape straw over the thermo-mechanical pretreatment using a continuous twin screw-driven reactor (CTSR). Bioresour. Technol. 130, 38–44.

Vandenbossche, V., Brault, J., Hernandez-Melendez, O., Evon, P., Barzana, E., Vilarem, G., Rigal, L., 2016. Suitability assessment of a continuous process combining thermo-mechano-chemical and bio-catalytic action in a single pilot-scale twin-screw extruder for six different biomass sources. Bioresour. Technol. 211, 146–153.

Velásquez-Cock, J., Gañán, P., Gómez H., C., Posada, P., Castro, C., Dufresne, A., Zuluaga, R., 2018. Improved redispersibility of cellulose nanofibrils in water using maltodextrin as a green, easily removable and non-toxic additive. Food Hydrocoll. 79, 30–39.

Yano, H., Nakahara, S., 2004. Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network. J. Mater. Sci. 39, 1635–1638.

Zhang, L., Lu, H., Yu, J., Wang, Z., Fan, Y., Zhou, X., 2017. Dissolution of lignocelluloses

with high lignin content in a NMMO/H $_2$ O solvent system via a simple glycerol swelling and mechanical pretreatment. J. Agric. Food Chem. acs.jafc.7b03429.

Zhang, Y., Hou, T., Li, B., Liu, C., Mu, X., Wang, H., 2014. Acetone-butanol-ethanol production from corn stover pretreated by alkaline twin-screw extrusion pretreatment. Bioprocess Biosyst. Eng. 37, 913–921.

Zhen, L., Zhang, G., Huang, K., Ren, X., Li, R., Huang, D., 2016. Modi fi cation of Rice Straw for Good Thermoplasticity via Graft Copolymerization of ε - Caprolactone onto Acetylated Rice Straw Using Ultrasonic-Microwave Coassisted Technology.

Zheng, J., Rehmann, L., 2014. Extrusion pretreatment of lignocellulosic biomass: A review. Int. J. Mol. Sci. 15, 18967–18984.

## Table and figure Captions

**Table 1** Solids content changes of wet mechanical pulps after 5 and 7 passes of twin-screw extrusion.

**Fig. 1.** Screw configurations with conveying elements and 90º offset kneading blocks for the pre-treatment of mechanical pulp.

**Fig. 2.** Water retention values of the mechanical wood pulps before and after twin-screw extrusion at different solids content.

**Fig. 3.** Photographs of the raw material (a) and mechanical pulps after extrusion at 30 wt% (b), 60 wt% (c) and 70 wt% (d) for 5 times.

**Fig. 4.** Light microscopy images of the original mechanical pulp (a), sample $SP_{30\text{-}5}$ (b), $SP_{60\text{-}5}$ (c), $SP_{60\text{-}7}$ (d), $SP_{70\text{-}5}$ (e) and $SP_{70\text{-}7}$ (f).

**Fig. 5.** SEM images of wood pulps after twin-screw-extrusion at 60 wt% for 5 times, $SP_{60\text{-}5}$ (a) and 70 wt% for 7 passes, $SP_{70\text{-}7}$ (b).

**Fig. 6.** Typical sedimentation of the twin-screw extrusion treated pulp (after five passes) aqueous suspensions after free-standing for 4 hours (a) and 24 hours (b), and the ratios between the sediment height and total suspension height after 24 hours.

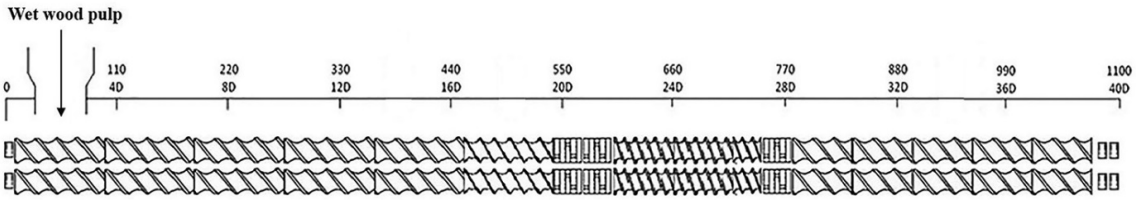
**Fig. 7.** Specific surface areas of the original mechanical pulp and after extrusion at 20 wt%), 30 wt%, 40 wt%, 50 wt%, 60 wt% and 70 wt% for 5 and 7 passes, respectively.

**Fig. 8.** Acetylation of the mechanical pulps before and after twin-screw pre-treatment.

**Table 1**

Solids content changes of wet mechanical pulps after 5 and 7 passes of twin-screw extrusion.

| Samples | Before extrusion (wt%) | Solid contents at Pass 5 (wt%) | Solid contents at Pass 7 (wt%) | Total solid content changes (wt %) |
|---|---|---|---|---|
| $SP_{20}$ | 20 | 21.47 ± 0.53 | 22.61 ± 0.79 | 2.61 ± 0.69 |
| $SP_{30}$ | 30 | 31.30 ± 0.11 | 33.54 ± 0.56 | 3.54 ± 0.56 |
| $SP_{40}$ | 40 | 42.30 ± 0.48 | 44.08 ± 0.92 | 4.08 ± 0.92 |
| $SP_{50}$ | 50 | 54.21 ± 0.014 | 56.62 ± 0.65 | 6.62 ± 0.65 |
| $SP_{60}$ | 60 | 63.59 ± 0.06 | 67.69 ± 2.29 | 7.69 ± 2.29 |
| $SP_{70}$ | 70 | 71.14 ± 1.52 | 78.25 ± 0.50 | 8.25 ± 0.50 |

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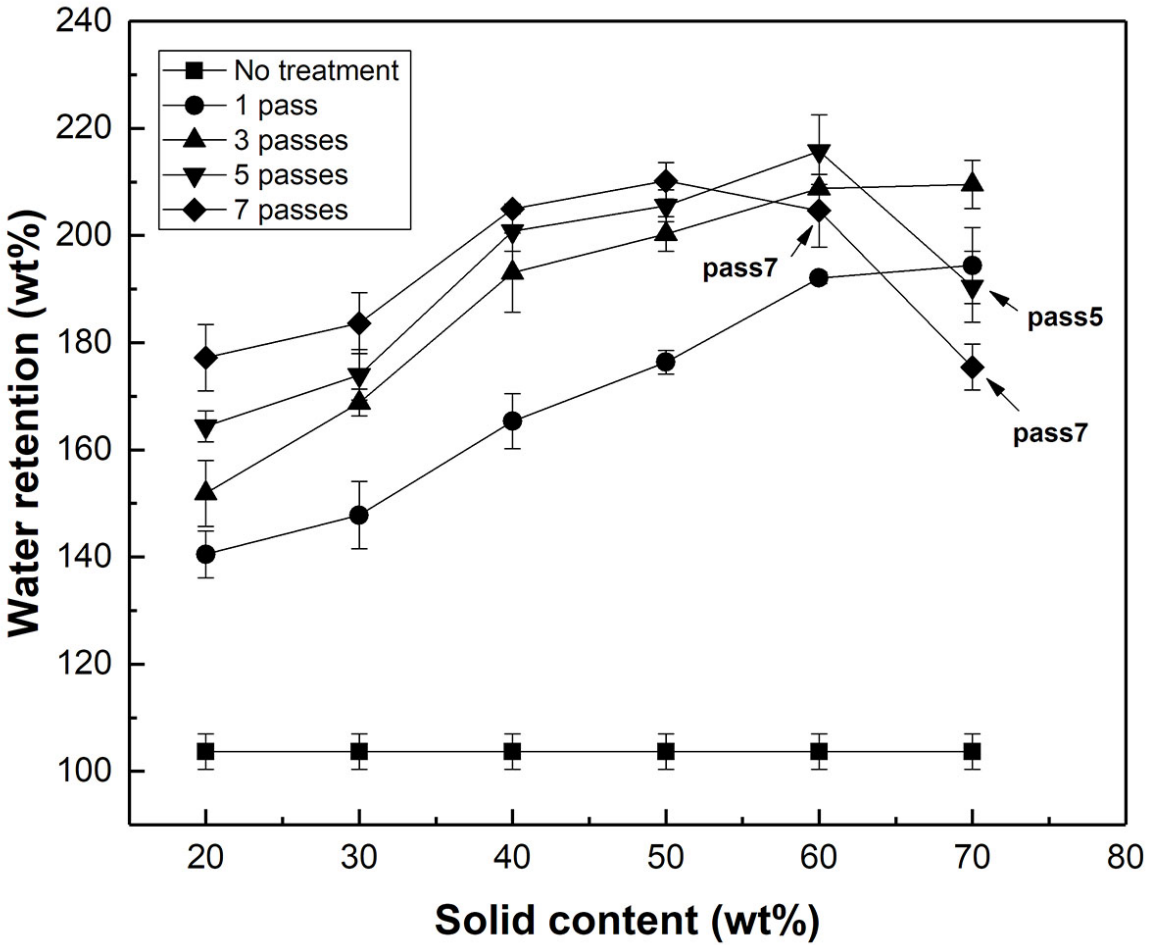


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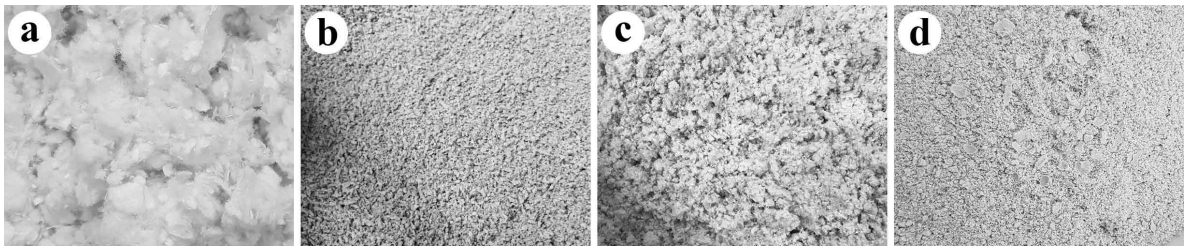


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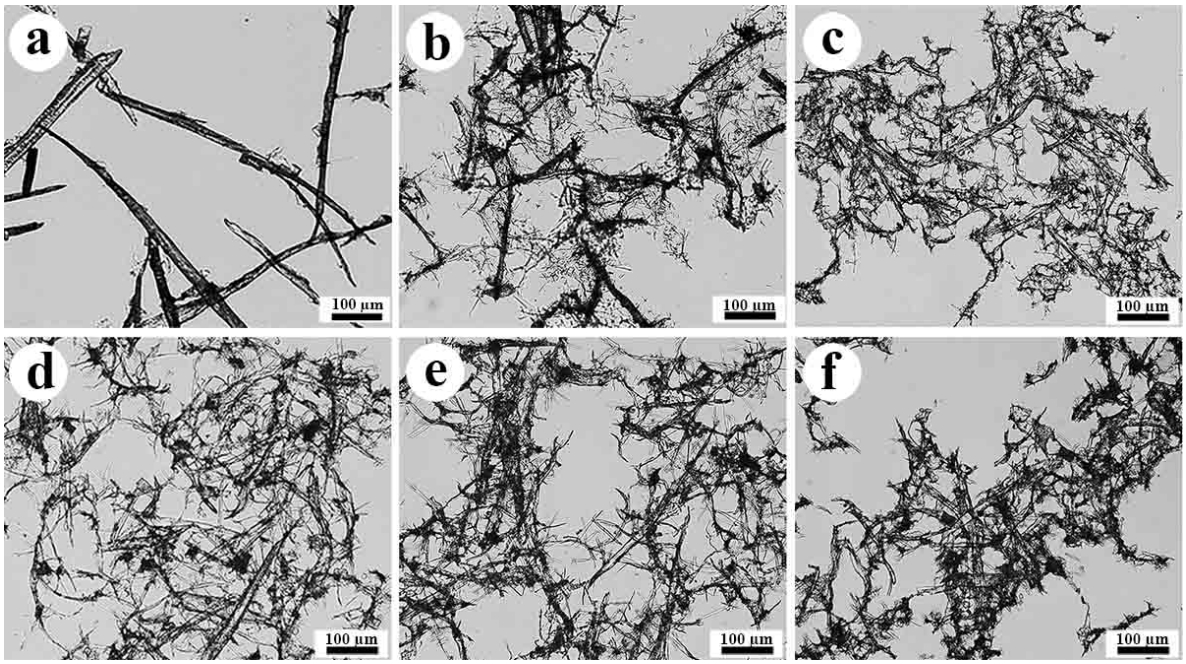


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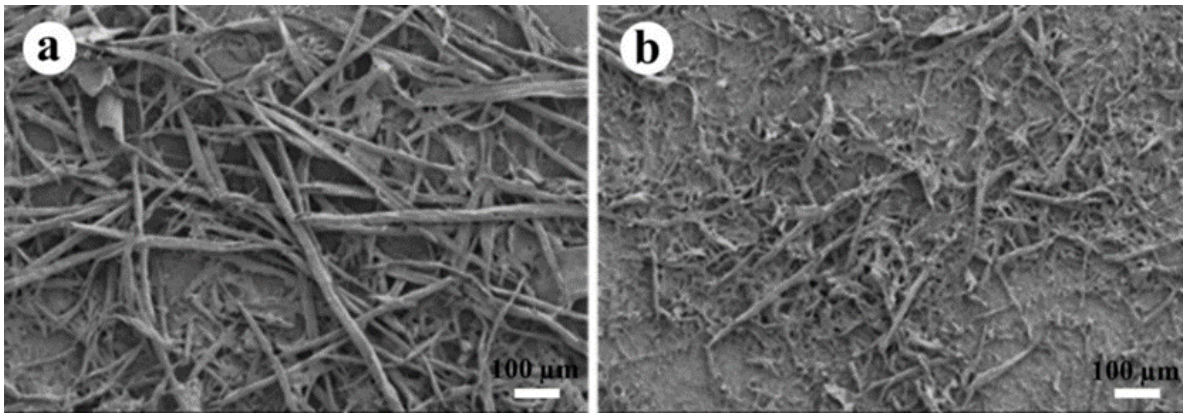


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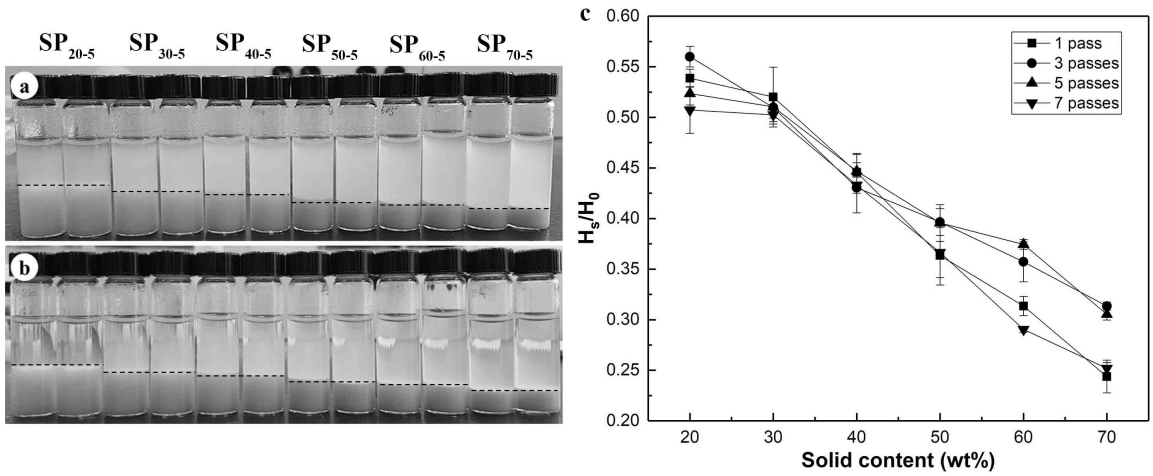


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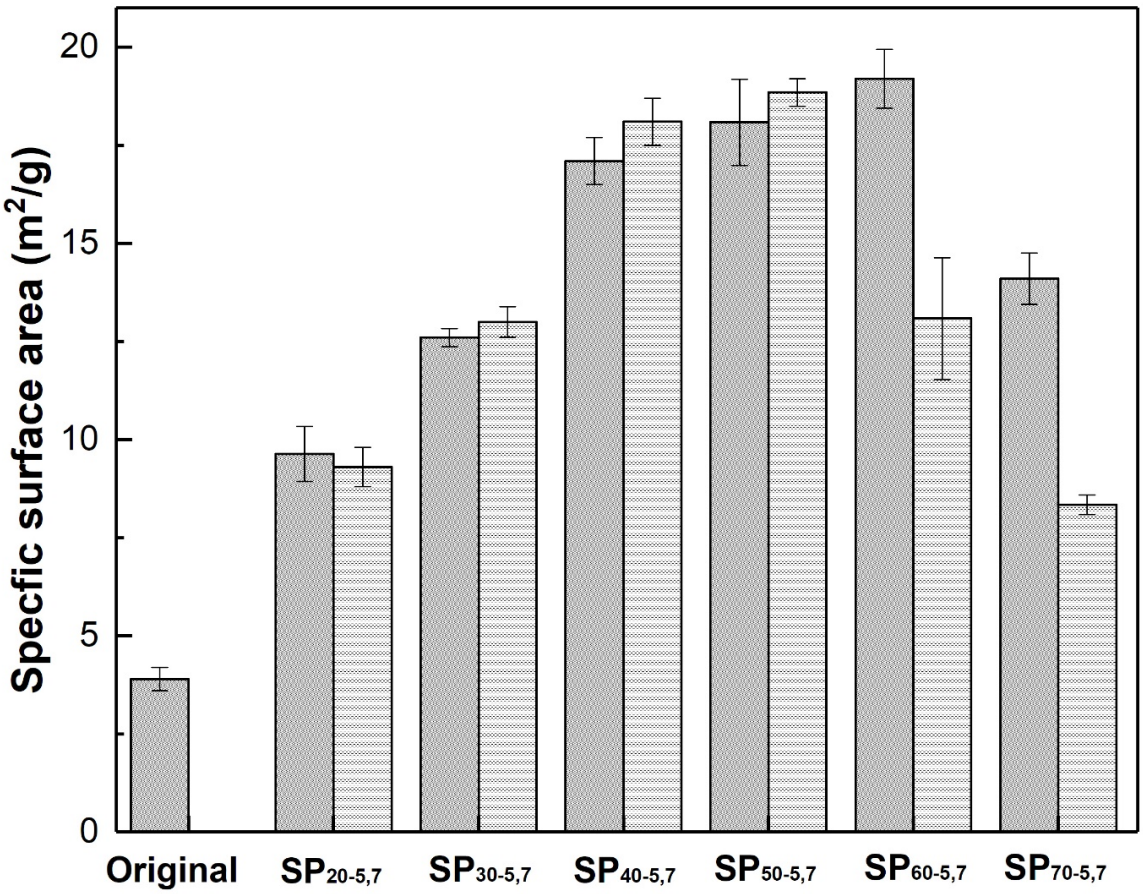


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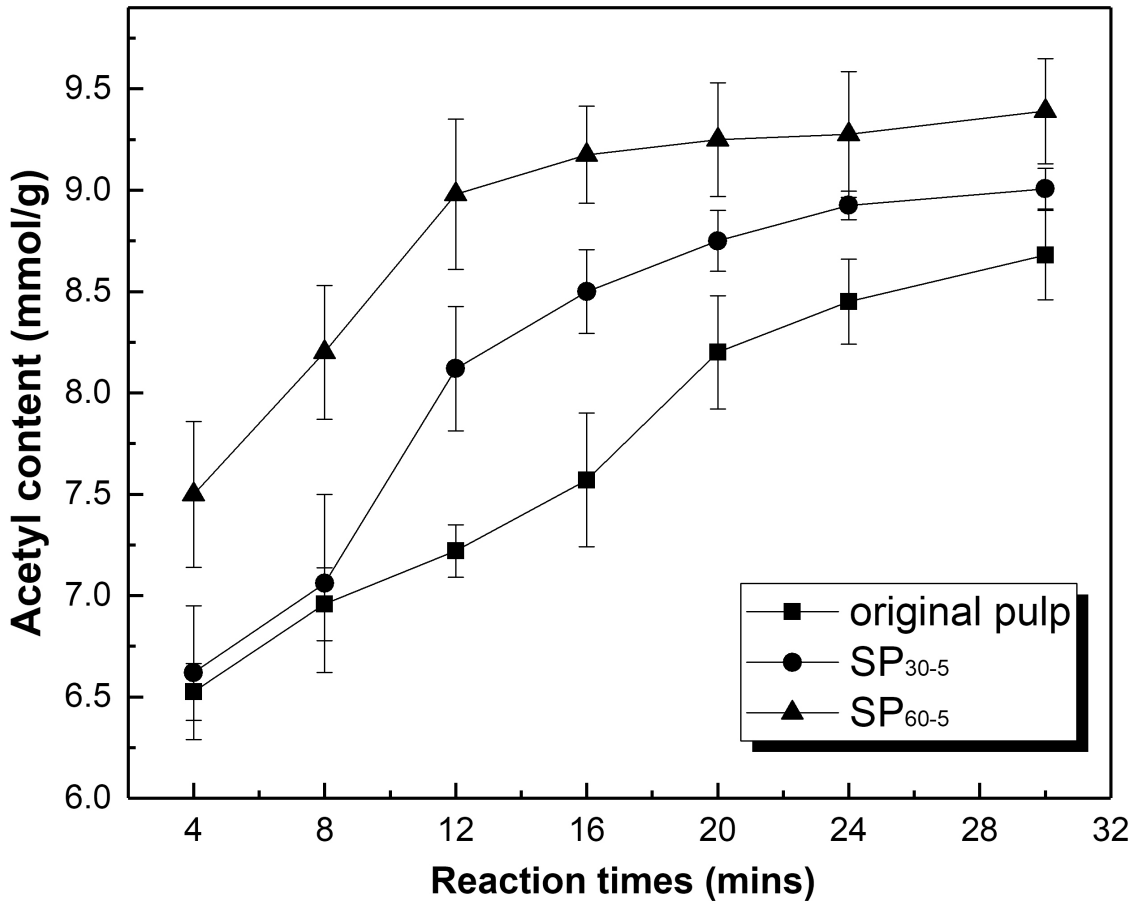


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