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Effects of Operating Parameters on Countercurrent Extraction of Hemicellulosic Sugars from Pretreated Softwood

KYOUNG HEON KIM, MELVIN P. TUCKER, AND QUANG A. NGUYEN*

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401-3393, E-mail: quang_nguyen@nrel.gov

Abstract

In a previous study using a continuous countercurrent screw extractor for two-stage dilute-acid hydrolysis, which was focused on the effects of liquid-to-insoluble solids (L/IS) ratio, we demonstrated that by using low volumes of wash water soluble sugars can be recovered from first-stage pretreated softwood at high yields and also at high sugar concentrations. In this study, we investigated the effects of important operating parameters other than the L/IS ratio, such as the feed rates of water and pretreated biomass and the extractor inclined angle, on the performance of the extractor using first-stage pretreated softwood. As biomass and water feed rates increased at the same L/IS ratio, the recovery yield of soluble sugars decreased, probably owing to a reduced solids residence time in the extractor, which is related to the solid/liquid contact time. The sugar recovery yield was higher at a higher extractor inclined angle. This may be attributed to the effects of increased back mixing and a longer residence time for solids at a higher extractor angle. Countercurrent extraction was also carried out with other pretreated biomass having smaller particle sizes and poor drainage rates. The countercurrent screw extractor was found to be unsuitable for these fine materials due to the slow liquid drainage rate and filter-clogging problems. In a test for stability of soluble sugars in first-stage softwood hydrolysate, irrespective of the storage temperature and storage form, the sugar concentration slowly decreased with storage time. However, storage in slurry form showed higher sugar stability compared with that in liquor form at the same conditions.

*Author to whom all correspondence and reprint requests should be addressed.

Index Entries: Continuous countercurrent extraction; hemicellulosic sugars; softwood; pretreatment; two-stage dilute-acid hydrolysis.

Introduction

Because it is well known that continuous countercurrent extraction offers minimal solvent usage and recovery of solutes at high concentrations *(1)*, continuous countercurrent extractors are commonly used in the food processing industry to separate soluble fractions from various kinds of feedstocks *(2–10)*. In two-stage dilute-acid hydrolysis of softwood, high recoveries of soluble sugars at high concentrations from first-stage hydrolysate are essential for process economics associated with ethanol production *(11–14)*. In our earlier study using a prototype continuous countercurrent extractor, we showed that high recovery yields of soluble sugars at high concentrations from first-stage pretreated softwood could be achieved using low amounts of wash water *(13)*. Solubles recovery yields of 77, 91, and 98% were obtained from first-stage pretreated softwood at liquid-to-insoluble solids (L/IS) ratios of 2.1, 3.4, and 5.6, respectively. In addition to the L/IS ratio, the wash water temperature was also found to significantly affect the solubles recoveries in bench-scale experiments.

As a follow-up to the previous study, we investigated the effects of other important operating parameters on the extractor performance such as feed rates of water and biomass and the inclined angle of the extractor. Additionally, the feasibility of using the continuous extractor for other pretreated materials having fine particle sizes was evaluated using two kinds of pretreated yellow poplar, that were acid hydrolyzed at more severe conditions than the first-stage pretreated softwood. We also investigated the stability of sugars in the softwood hydrolysate because the pretreated biomass samples are usually stored for certain periods until they are further processed. We reported herein the changes in monomeric sugar concentration during storage of hydrolysates.

Materials and Methods

Acid Impregnation of Softwood for First-Stage Pretreatment

Whole-tree chips from California softwood forest thinnings composed of 70% white fir and 30% ponderosa pine *(15)*, that had been milled to pass through a 0.5-in. screen, were soaked in 0.8% (w/w) H_2SO_4 solution at 50°C for 4 h. The acid-impregnated softwood chips were then partially air-dried to 43% (w/w) of total solids content at approx 30°C using a rotary dryer. To measure the final acid concentration of liquid entrained inside the partially dried softwood chips, 100 g of softwood chips was extracted with 1000 mL of deionized water at 40°C with shaking overnight. The extracted acid solution was titrated with 0.5 *N* standard NaOH solution (J. T. Baker, Phillipsburg, NJ), and the final acid concentration of the liquid inside the partially dried wood chips before pretreatment was found to be 1.1% (w/w). In this article, all the H_2SO_4 concentrations of softwood feedstocks enumerated under conditions of pretreatment are expressed as acid concentrations of entrained liquid in the partially air-dried feedstock.

First-Stage Pretreatment of Acid-Soaked Softwood

The acid-soaked and partially dried softwood chips were pretreated at 185°C for 4 min using a 4-L steam explosion reactor described previously *(11)*. The soluble sugar yields (percentage of theoretical maximum yield of total soluble sugars including both monomeric and oligomeric forms) from the pretreatment were 90% from nonglucose hemicellulose and 13% from glucan. In the first-stage pretreatment of softwood, the conversion yield of cellulose was much lower than that of hemicellulose because the relatively mild pretreatment conditions, compared with second-stage pretreatments, which were aimed at maximizing soluble hemicellulose sugar yield. Typical results of softwood first-stage pretreatments at the same pretreatment condition (1.1% H_2SO_4 and 185°C for 4 min) can be found in our previous report *(13)*.

Pretreatments of Other Feedstocks

To test the performance of the extractor with pretreated biomass consisting of fine particle sizes and to establish the relationship between the packed-biomass bed volume reduction and the water drainage rate using these fine materials, two different pretreated yellow poplar samples were obtained. Yellow poplar sawdust was pretreated at 0.3% (w/w) H_2SO_4 and 195°C for 5 min using a Sunds™ Hydrolyzer installed at the NREL pilot plant. The detailed pretreatment methods and results of this material are given elsewhere *(16)*. Yellow poplar chips (1-in. commercial pulp chip size) were pretreated at 0.55% H_2SO_4 and 170°C for 15 min using a Sunds Hydrolyzer installed at the Tennessee Valley Authority (TVA) pilot plant (Muscel Shoals, AL). The water-insoluble fraction of the pretreated yellow poplar chips from TVA was 72% on a dry wt basis, and the total soluble solids concentration of the liquid fraction of the pretreated material was determined to be 144.6 g/L by oven drying at 105°C overnight.

For drainage tests with second-stage pretreated softwood having fine particle sizes, first-stage pretreated softwood was washed thoroughly with water until the pH of the slurry increased to between 5.0 and 6.0, then the washed feedstock was acid–impregnated for pretreatment. The acid-soaked and dewatered biomass material (2.5% H_2SO_4 concentration) was then pretreated at 210°C for 2 min using the NREL steam explosion reactor as described previously *(11)*.

Test of Sugar Stability in Softwood Hydrolysate

After a large amount of first-stage pretreated softwood was produced, there existed a time gap before the pretreated material was used in the extraction experiments. Therefore, it was necessary to monitor the concentration change of each soluble sugar component in the hydrolysate during storage. Two different types of hydrolysate in whole slurry-form and in liquor form (pressed from slurry using an NREL custom-made hydraulic press composed of a cylinder with a 25.0-cm diameter and 30.5-cm height at an internal pressure of approx 600 psi) were stored at two different temperatures: 4 and –11°C. The plastic containers for the stored samples were tightly sealed with paraffin film to minimize possible water loss by evaporation during the long-term storage. The monomeric sugar analysis covering a period as long as 43 d for the stored liquors and slurries was conducted by high performance liquid chromatography (HPLC).

Bench-Scale Drainage Test

To find any relationship between the liquid drainage rate and the bed volume reduction of packed biomass, bench-scale percolation tests were performed using a silicone column and deionized water as described in our previous work *(13)*. The liquid drainage flux and the bed volume change after liquid drainage were measured with various materials including the untreated softwood chips, the first- and second-stage pretreated softwood, and the two pretreated yellow poplar samples.

Countercurrent Extraction of Pretreated Biomass

Extraction experiments were conducted using a pilot-scale continuous countercurrent extractor designed as in Fig. 1 by NREL. The detailed description of this unit and operating procedures are available elsewhere *(13)*. Process water was heated to 60°C in the water heater and circulated through the screw conveyor jacket. The temperature of wash water sprayed near the solids discharge opening at the top of the extractor remained steady during extraction. However, the steady-state temperature varied in the range of 54–58°C depending on the flow rate of wash water. At the beginning of a run, a constant volumetric biomass feedstock feeder (Acrison feeder BDFM, Acrison, Moonachie, NJ) set at a predetermined feed rate began to feed pretreated biomass into the bottom of the extractor. The introduced biomass mixed with water was conveyed to the top of the extractor by a screw auger set at a fixed rotational speed. The extracted liquid passing through coarse filters at the bottom of the extractor was collected in a flask connected to a vacuum pump. Each continuous extraction experiment lasted for approximately four times the solids residence time. The L/IS ratio, which is defined as the weight ratio of wash water flow rate over insoluble solids feed rate (dry wt basis), was kept constant during each extraction run.

Analyses of Solids and Liquid Samples

To determine the washing efficiency and soluble solids recovery yield from continuous extraction, the fraction of insoluble solids both in feed

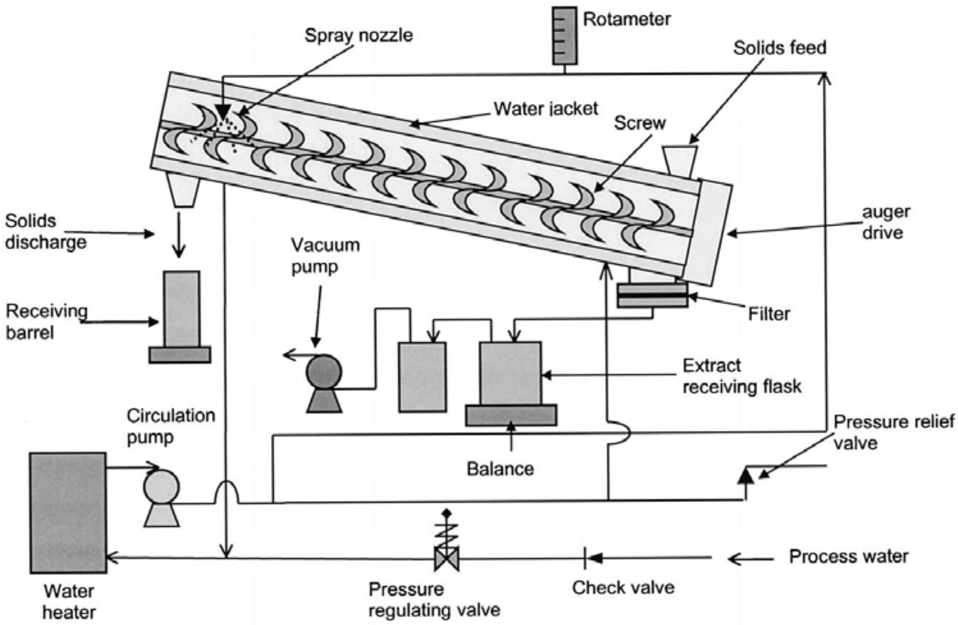

Fig. 1. Schematic diagram of pilot-scale continuous counter current extractor.

materials and in extracted solids was determined by extensive washing of solids samples with 40°C water. The detailed washing procedures and the method of determining the fraction of insoluble solids are described in a previous study *(13)*.

To obtain the liquid fraction from pretreated biomass samples and washed solids produced from extraction runs, solid samples were pressed using a hydraulic press fabricated at NREL as described earlier. The monomeric sugar concentration in the liquid samples was measured by HPLC using a lead-based cation-exchange column (Aminex HPX-87P; Bio-Rad, Hercules, CA) *(17)*. Each sample was neutralized with calcium carbonate and filtered with a 0.2 μm membrane filter prior to injecting on the HPLC column.

Results and Discussion

Stability of Soluble Sugars in Softwood Hydrolysates

To investigate the stability of soluble sugars contained in the first-stage pretreated softwood hydrolysate, the monomeric sugar concentrations of each hydrolysate stored at both 4 and –11°C in two different forms (whole slurry and pressed liquor) were measured by HPLC at various time intervals, as shown in Fig. 2. Among the three major sugar components of the softwood hydrolysate presented in Fig. 2, glucose showed the most rapid decrease in concentration during the 43-d storage period. However, the concentrations of mannose and xylose slowly decreased with time.

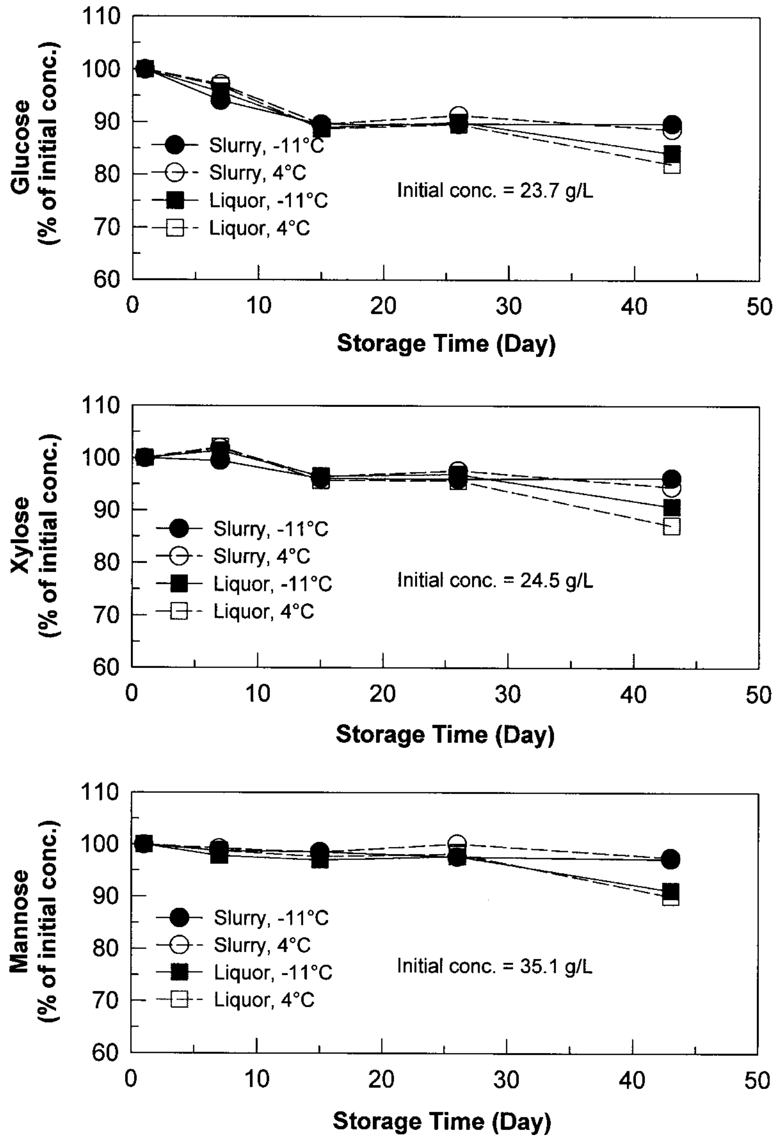

Fig. 2. Normalized concentration changes of monomeric sugars in first-stage pretreated softwood with storage time under different storage methods and temperatures.

Storage of the samples up to periods of 26 d gave similar decreasing concentrations of each sugar component regardless of storage temperature and method. However, when the storage period was increased to 43 d, the sugar concentration decreased by 9–18% depending on sugars for the samples stored in liquor form at both temperatures. In the slurry form, the losses of soluble sugars (4–11% after 43 d) were less pronounced than those found in the liquid form.

Bench-Scale Drainage Test

Depending on the particle size of input feedstocks and various pretreatment conditions, the particle size of pretreated biomass residues will differ for each pretreatment. If the particle size of pretreated biomass is too small, it may become muddy when mixed with water and have poor solid/liquid (S/L) separation, low water-drainage rates, and packing problems after water drainage. These can be serious obstacles for the operation of continuous screw extractors. To evaluate the liquid drainage characteristic of each biomass sample before testing with the pilot-scale continuous extractor, bench-scale drainage experiments using a percolation column were conducted. In these experiments, the drainage flux and the change in biomass bed height were measured.

Figure 3 shows that a strong negative correlation ($R^2 = 0.99$) exists between the mass flux of liquid drain and the bed volume reduction after liquid drainage. The untreated softwood chips showed the highest drainage rate. The yellow poplar and the second-stage softwood, which were pretreated under more severe conditions than the first-stage softwood, showed lower drainage rates. This indicates an inverse correlation between the drainage flux and the severity of pretreatment. As can be seen in Fig. 3, the untreated softwood feedstock, the first-stage softwood, and the severely pretreated wood including the yellow poplar and second-stage softwood showed bed volume reductions of 8, 33, and 43–46%, respectively. The more the bed was compacted, the lower the observed liquid drainage flux. Therefore, substantial bed compaction caused by the fine particles probably led to the lower liquid drainage rates for the severely-pretreated biomass materials. A similar bed compaction problem with fine particles was also reported by others in the extraction of soybean oil from fine soybean flour using an extraction column *(18)*.

Time Course of Countercurrent Extraction Run

Figure 4 shows a typical time course of continuous countercurrent extraction of first-stage pretreated softwood. The extraction was carried out at an L/IS ratio of 2.1. Feed rates of wash water and biomass were 175 and 206 g/min, respectively. The inclined angle of the extractor was set at 60° from horizontal. Typically washed solids begin to exit the extractor 50 min after the start-up of extraction. The time counted from the start-up of the run to the beginning of washed solids discharge was longer than a single solids residence time determined at steady state, because the bottom section of the extractor needs to be filled with solids before conveyed material appears at the top for discharge. Washed solids samples taken at certain time intervals showed steady values of soluble recovery yield with extraction time as given in Fig. 4.

Table 1 lists the sugar composition of the hydrolysate liquor pressed from the first-stage pretreated softwood, the liquid extract, and the liquid

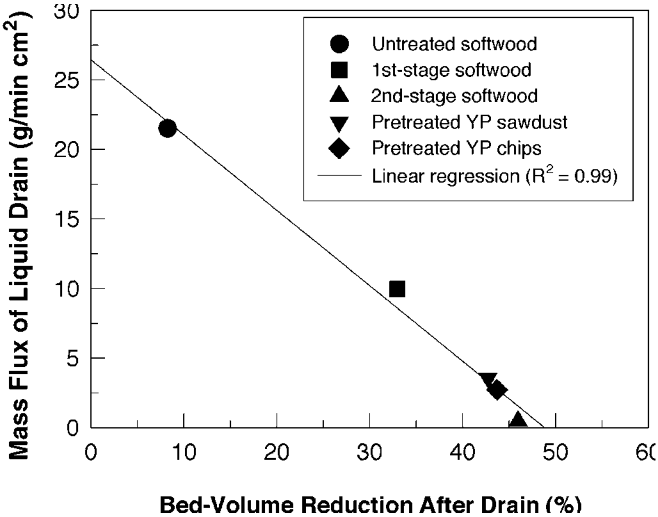

Fig. 3. Correlation between percentage of bed volume reduced after water drainage and mass flux of water in bench-scale drainage test with untreated softwood, first- and second-pretreated softwood, and pretreated yellow poplar (YP) sawdust and chips.

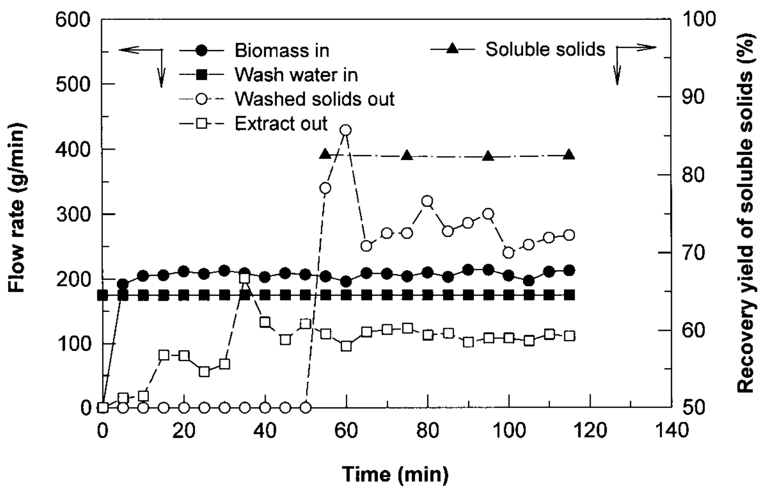

Fig. 4. Typical time course of continuous countercurrent extraction of soluble solids from first-stage pretreated softwood at L/IS = 2.1, feed rates of 175 g/min for wash water and 206 g/min (based on wet wt) for pretreated biomass, and 60° inclined angle of extractor from horizontal.

fraction of washed solids, which were obtained from the continuous extraction run shown in Fig. 4. Because of the low L/IS ratio (L/IS = 2.1), the dilution effect caused by added wash water was small, as reflected by the high sugar concentration of the liquid extract shown in Table 1.

Table 1
Sugar Composition of Liquid Fractions of Starting Pretreated Softwood, Liquid Extract, and Washed Solids from Continuous Countercurrent Extraction at L/IS = 2.1

	Monomeric sugar concentration (g/L)[a]				
Liquid fraction	Glucose	Xylose	Galactose	Arabinose	Mannose
Hydrolysate liquor	18.7 ± 0.0	20.7 ± 0.1	9.9 ± 0.1	7.6 ± 0.0	30.5 ± 0.1
Extract	13.3 ± 0.4	16.4 ± 0.0	7.8 ± 0.0	6.2 ± 0.2	27.8 ± 0.4
Washed solids	2.4 ± 0.1	3.3 ± 0.0	2.0 ± 0.0	1.2 ± 0.0	4.5 ± 0.0

[a] Standard deviations for the sugar composition by HPLC analysis ranged from 0.0 to 0.4 g/L.

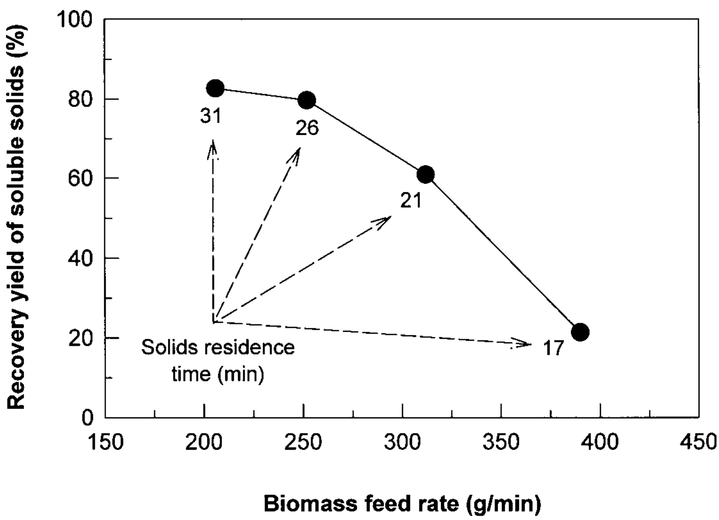

Fig. 5. Effect of biomass feed rate and solids residence time on recovery of soluble solids in continuous countercurrent extraction of sugars from first-stage pretreated softwood at L/IS = 2.1.

Effects of Biomass and Wash Water Feed Rates

One advantage of the continuous countercurrent extractor is a high throughput owing to continuous operation. We studied the effects of feed rates of biomass and wash water on the performance of continuous extraction since the biomass and water feed rates directly affect the processing capacity of the continuous extractor. As shown in Fig. 5, the extraction with the first-stage pretreated softwood was carried out at four different feed rates of biomass and wash water with L/IS = 2.1 and a screw auger speed of 20 rpm. The soluble sugar recovery is directly proportional to the recovery of soluble solids.

The feed rate was found to have a significant impact on the solubles recovery yields even at a fixed L/IS ratio. Varying the feed rate resulted in different solubles recovery yields in a range as wide as 21–83%. As the feed rate increased, the yields of extracted solubles significantly decreased.

The average solids residence time was determined by the average volume of solids filling the conveyor and the average volumetric solids feed rate. As seen in Fig. 5, the average solids residence time was found to be inversely proportional to the biomass solids feed rate. Based on the relationship between the solids feed rate and residence time, the soluble solids recovery yields were found to decrease with a shorter solids residence time. Since the auger speed was fixed at 20 rpm, a lower solids feed rate led to longer S/L contact time and better solubles recovery because the rate and extent of diffusion are proportional to the contact time in washing solids *(19)*.

Effects of Inclined Extractor Angle

Since the downward flow of extraction liquor containing soluble sugars was driven by gravity, the extractor was mounted at an inclined angle from horizontal. The extent of extract liquid channeling and the solids-conveying rate are thought to be affected by the inclined conveyor angle. Therefore, to investigate the effect of extractor angle on the extraction, extraction experiments were conducted at different inclined angles of 40, 50, and 60° from horizontal by fixing other operating conditions (screw auger speed = 20 rpm, L/IS = 2.1, biomass feed rate = 200 g/min, and water flow rate = 175 g/min).

Figure 6 displays the effect of inclined extractor angle on the solids residence time and solubles recovery yield. As the angle of the inclined extractor increased, the solubles recovery yield increased as did the solids residence time. The screw conveyor was filled with increasing amounts of solids at higher inclined angles, resulting in longer solids residence times. The back mixing of solid and liquid was observed to be more pronounced at an inclined angle of 60° than at 40° and 50°. As a result, longer S/L contact times and back mixing of solid and liquid may be the primary reasons for a higher solubles recovery at higher incline angles.

Extraction Runs with Pretreated Yellow Poplar

The development of continuous countercurrent extraction was intended for soluble solids recovery from first-stage pretreated softwood prior to second-stage dilute-acid hydrolysis. However, the feasibility study for the continuous countercurrent extractor was extended to pretreated biomass containing much smaller particles than the first-stage pretreated softwood. For this purpose, the pretreated yellow poplar sawdust (pretreated at NREL) and yellow poplar chips (pretreated at TVA) were tested with the NREL continuous countercurrent extractor. The L/IS ratio was maintained at 2.1.

In extraction of biomass materials containing fines, it was observed that powder-like fine materials easily clogged the filtration system located

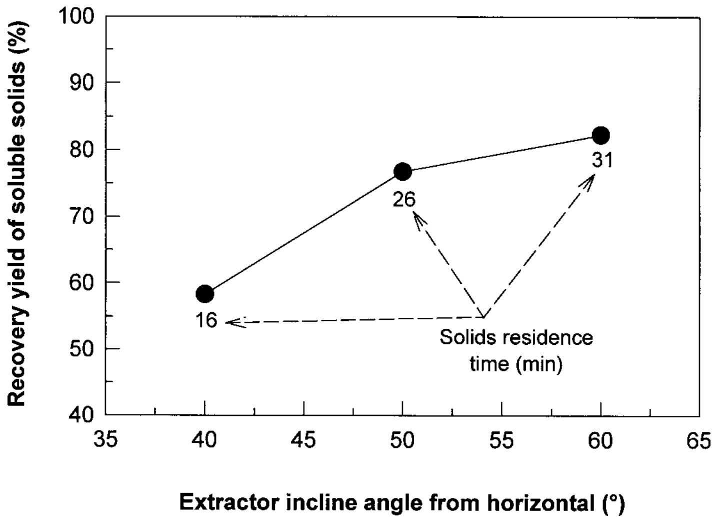

Fig. 6. Effect of incline angle of extractor on recovery of soluble solids in continuous countercurrent extraction of first-stage pretreated softwood at L/IS = 2.1.

at the bottom of the extractor. As seen in Fig. 7, during extraction of the pretreated yellow poplar chips, the flow rate of extract liquid decreased rapidly with extraction time. As a result, filters needed to be replaced in less than 30 min after start-up, due to a serious decrease in liquid extract flow rate. As the number of filter replacements increased, the initial maximum extract liquid flow rate decreased. The results indicate that poor drainage through the bed is the result of small biomass particles accumulating in the chute leading to the filters at the bottom of the extractor. These small particles passed through a screen (1/16-in. perforated plate) welded to the top of the chute. Therefore, the frequent replacement of filters did not entirely solve the slow drainage problem. The accumulation of biomass in the chute also occurred during the extraction of the first-stage pretreated softwood. However, despite the accumulation of biomass fines, the extract flow rate did not decrease significantly due to the high water drainage characteristic of the first-stage softwood material, as presented in Fig. 3.

The plugging problem with the pretreated yellow poplar materials occurred not only in the filtration system but also in the extractor trough. The slow liquid drainage through the accumulated biomass in the lower part of the extractor caused flooding in the feed part of the extractor. Thus, the screw could not effectively convey the solids in the flooded section to the top of the extractor. This is shown in Fig. 7, where no sign of discharged solids was found 70 min after starting the extraction run. By comparison, the extraction runs with the first-stage pretreated softwood showed discharge of washed solids after 25–50 min, depending on the operating conditions. Eventually, the feed chute at the bottom of the extractor was overfilled with the pretreated yellow poplar feed materials, thus disabling

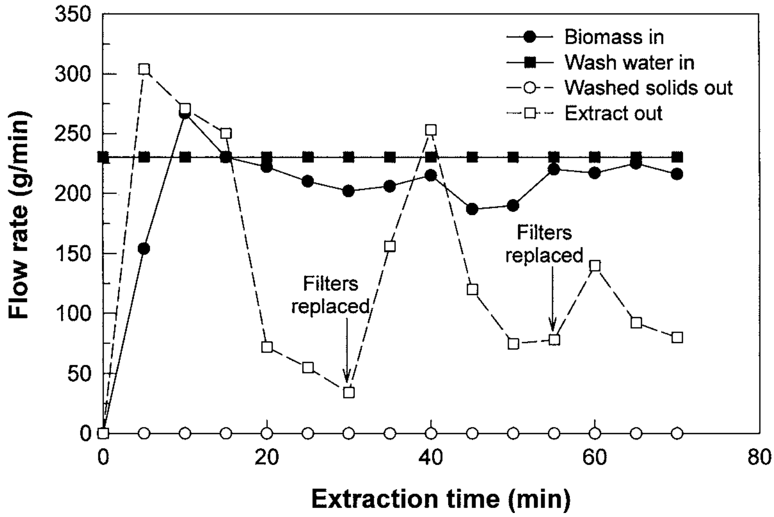

Fig. 7. Continuous countercurrent extraction of pretreated yellow poplar chips with fine pretreated particles.

the extraction. We also observed separation of materials in the TVA-pretreated yellow poplar run. The fines were washed down to the lower section of the extractor. Coarse chips were conveyed to the upper sections. Toward the end of the run, the fines had accumulated at the bottom of the extractor trough, forming a wet muddy mass, which was simply churned but not conveyed upward.

As seen earlier in Fig. 3, the poor drainage of yellow poplar materials was also observed in the bench-scale percolation experiment. Therefore, the current design and setup of this screw extractor is not suitable for fine particles, such as found in pretreated yellow poplar and second-stage softwood, because of their slow drainage properties. One possible solution for processing materials with poor drainage properties and containing large amounts of fines is to improve drainage by enlarging the filtering section. One example of this application is the perforated trough design used in the pulp industry. In this case, the extraction would not be truly countercurrent because a significant portion of wash water would bypass the pulp. As a result, such a design would negatively affect the solubles recovery yield and the L/IS ratio. Furthermore, a solid/liquid separation unit operation would be required to recover the large amount of fines passing through the perforated trough.

Conclusion

In continuous countercurrent extraction of hemicellulosic sugars from first-stage pretreated softwood, the feed rates of water and pretreated biomass and the extractor inclined angle were found to have significant effects on performance of the extractor. At a fixed L/IS ratio, as feed rates of water and biomass increased, recovery yields of soluble solids decreased. At the same feed rates of wash water and biomass, a solubles recovery yield was found to be higher with an increase in the extractor inclined angle. At the various feed rates and inclined angles tested, the soluble recovery yields ranged from 21 to 82% at a fixed L/IS of 2.1.

The current configuration of the screw extractor was found to be unsuitable for processing pretreated materials containing predominantly fine particles. These pretreated biomass residues showed slow drainage rates in a bench-scale packed-bed system.

In a sugar stability test with first-stage softwood hydrolysate, the monomeric sugar concentration was found to slowly decrease with storage time regardless of storage temperature and form (e.g., whole slurry or pressed liquor from slurry). Sugars appeared to be more stable when stored in a slurry form, as compared with sugars of liquor pressed from slurry and stored at the same storage temperature and length of time.

Acknowledgment

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