CELLULOSE CHEMISTRY AND TECHNOLOGY

PREPARATION OF BIODIESEL AND SEPARATION OF HEMICELLULOSE FROM SOAP SKIMMINGS

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Soap skimmings are an intermediate substrate in the production of tall oil from Kraft pulping black liquor. In this study, biodiesel was produced directly from soap skimmings before being processed into tall oil using acetyl chloride and sulfuric acid as accelerators. The effects of the accelerator amount, reaction time, and pH on the production yield were investigated. The yields of biodiesel reached 35%, and the hemicellulose by-product could be separated during the process and could be used as a chemical stock for other applications (e.g., carboxymethylated hemicellulose and biofuels).

Keywords: biodiesel, soap skimmings, tall oil, reaction catalyst, hemicellulose

INTRODUCTION

Biodiesel is made from vegetable oil and tallow, but the consumption of these products affects the supply chain of food. As a raw material outside the food supply chain, the authors chose pulping black liquor, especially tall oil. Tall oil is a viscous, yellow-black, odorous liquid obtained as a by-product of the Kraft process of coniferous tree pulp manufacturing[1-2] requiring special utility vehicles for being transported from the mill site, which makes the entire transportation process costly and cumbersome. As a result, Kraft pulping mills have to sell crude tall oil at a very low price.[3-4]

Tall oil is the third largest chemical by-product in a Kraft mill after lignin and hemicellulose. The yield of crude tall oil from the process is in the range of 30-50 kg/ton of pulp.[5] Tall oil can be used as a raw material for biodiesel production, and yields over 50% can be obtained.[6] Soap skimmings are an intermediate product of tall oil and are naturally separated from black liquor in the pulping process. As a natural product, soap skimmings contain various compounds, including a mixture of fatty and rosin acid salts and other neutral components. Soap skimmings are less expensive than tall oil. If the production of biodiesel can be initiated from soap skimmings, the cost could be reduced tremendously because the collection method of soap skimmings is relatively easy, i.e., evaporation to the appropriate status, storing in a setting tank and separating the soap skimmings and waste liquid.[4] Tall oil preparation, as the next process, requires large capital input to build an acid-resistant reactor for strong acid treatment. In this study, the production of biodiesel from soap skimmings was investigated.

EXPERIMENTAL

Soap skimmings and chemicals

Soap skimmings (water content 33%, pH 9.5-10) were provided by a North American Pulp Mill (main species is spruce). Sulfuric acid, acetyl chloride, methanol, and ethyl acetate were all of analytical grade and were provided by Sigma Aldrich Co. Ltd.

Esterification of soap skimmings

Using acetyl chloride as a catalyst

Soap skimmings (150 g) were suspended in 400 mL of methanol. Next, 30 mL of acetyl chloride was added at room temperature. After plugging, the solution was stirred for 1 h at 55 °C. Methanol was recovered by vacuum evaporation. The residue was dissolved in 400 mL ethyl acetate and was washed with water three times (200 mL x 3). The ethyl acetate fraction was dried with anhydrous sodium sulfate, and the solvent was recovered by a rotary evaporator. The residue was fractionated by vacuum distillation.

Using sulfuric acid as a catalyst

Soap skimmings (150 g) were suspended in 300 mL of methanol, and 20 mL of concentrated sulfuric acid was added. After plugging, the solution was stirred for 1 h at 65 °C. Methanol was recovered by vacuum evaporation. The residue was dissolved in 400 mL of ethyl acetate and was washed with water three times (200 mL x 3). The ethyl acetate phase was dried with anhydrous sodium sulfate and was concentrated by a rotary evaporator. The residue was fractionated by vacuum distillation.

Vacuum distillation

The esterification products, prepared using the procedure described above, were fractionated by vacuum distillation. The esterified product was transferred into a 500 mL round-bottom flask equipped with a vacuum distillation unit composed of a trap, thermometer, condenser, and receiving unit. Distillation was performed to obtain the following fractions: below 160 °C, 160 °C-200 °C, and over 200 °C (under vacuum: 2 mmHg).

Analysis of biodiesel by gas chromatography

Biodiesel, refined as described above, was analyzed by gas chromatography using a Hewlett Packard Model 5890 GC with a capillary column (EC-1, 30 m×0.25 mm, Alltech Corp). The operating conditions were as follows: injector temperature: 150 °C, detector temperature: 270 °C, initial temperature: 80 °C, holding time: 1 min, rate of temperature increase: 2 °C/min, final temperature: 250 °C, holding time: 5 min. Biodiesel prepared from vegetable oil was also analyzed and compared with that obtained from soap skimmings.

pH measurements

Because the pH of the reaction mixture cannot be conveniently measured, the pH of the wash water was measured.

Separation of hemicellulose from soap skimmings

The water phase (200 mL x 3 = 600 mL) described above (in *Using sulfuric acid as a catalyst*) was allowed to stand for 2-3 days with occasional shaking. The floating hemicellulose was slowly precipitated with the evaporation of ethyl acetate, and the precipitate was filtrated and collected. The filtrate was evaporated to approximately 300 mL and was mixed with 300 mL acetone under stirring. After standing, additional precipitate was collected. The flow sheet of solvent fractionation is shown in Figure 1.

Carboxymethylation of hemicellulose

Hemicellulose samples (600 mg) were mixed with 33 mL of 2-propanol in an Erlenmeyer flask (125 mL). Under magnetic stirring, 1 mL of 30% NaOH was added to the mixture, followed by 450 mg of monochloroacetic acid (MCA). Then, the mixture was heated via an oil bath at 55 °C for 4 h. The cooled mixture was separated into the solvent and solid phases using a centrifuge (at 3000 rpm). The insoluble material was washed several times with a solution of water/methanol (1:9 by volume) and then with methanol only. After drying over P_2O_5 in a vacuum oven, the yield of the resulting carboxymethylated hemicellulose (CMH) was determined.

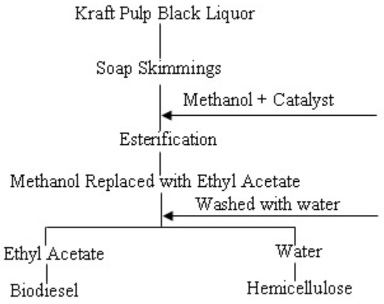


Figure 1: Flow sheet of solvent fractionation

Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structures of the CMH were evaluated by FT-IR spectroscopy. FT-IR spectra were obtained on an FT-IR spectrophotometer (Tensor 27) using a KBr disc containing 1% of the finely ground samples.

Scanning Electron Microscopy (SEM)

The particle surface features of hemicellulose and CMH were studied with a JEOL (JSM-6490A) SEM with an acceleration voltage of 30 kV. The sample surfaces were sputter-coated with gold to prevent charging.

Gel Permeation Chromatography (GPC)

The number and weight average molecular weights of CMH were determined using GPC on a Waters GPC system with a Waters Ultrahydrogel 120 column and a refractive index detector. Water was used as mobile phase (flow rate: 0.8 mL/min), and the analysis was performed at 25 °C. A universal calibration was used for the calculation of the molecular weights using a polyethylene glycol standard.

RESULTS AND DISCUSSION

Yields of products

Yield of biodiesel

Compared to the tall oil, the soap skimmings contained a large amount of impurities, including lignin and lignin-related compounds, an extractive component that could not be esterified, and pulp fines and other carbohydrates. The authors attempted to make tall oil from soap skimmings by solvent extraction and removed approximately 40% ±α of the impurities. From the tall oil prepared in the lab, we obtained almost the same amount of biodiesel (50% ±α). In addition, the biggest difficulty was that the soap skimmings also contained a significant amount of alkaline water (water content approximately 33%, pH 9.5-10). Additionally, in the process of esterification, fatty acids and resin acids, which have the potential to be converted to target materials, exist in the form of their organic salts. These factors significantly influence the catalyst. The esterification results with acetyl chloride and sulfuric acid catalysts are recorded in Table 1 and Table 2, respectively.

The biodiesel fuel yield was 34.5% (Exp. #9 in Table 1) and 35.2% (Exp. #5 in Table 2) after 0.5-1 h using acetyl chloride and sulfuric acid as catalysts, respectively. In previous studies using crude tall oil as raw material, the biodiesel yield was approximately 50%.[6]

Table 1
Esterification conditions and yields of biodiesels (with acetyl chloride)

Exp.#	Meth (mL)*	AcCl (mL)*	Temp. (°C)	Time (h)	Yield (%)	pH
1	600	100	25	24	41.5	N.M.*
2	600	100	55	1	37.7	1.0
3	600	100	55	6	36.7	N.M.
4	400	20	55	1	22.4	2.5
5	400	10	55	1	20.2	7.5
6	400	50	55	1	33.9	1.0
7	400	30	55	1	34.5	1.0
8	400	30	55	0.5	33.1	1.2
9	400	30	55	1	34.5	1.2
10	400	30	55	3	35.7	1.2
11	400	30	55	6	36.2	1.2
12	400	30	55	10	37.5	1.2

Table 2
Esterification conditions and yields of biodiesels (with sulfuric acid)

Exp.#	Meth (mL)*	H_2SO_4(mL)	Temp. (°C)	Time (h)	Yield (%)	pH
1	400	10	65	1	30.7	1.8
2	400	30	65	1	33.5	1.3
3	400	5	65	1	0.1	8.7
4	400	20	65	1	33.7	1.3
5	300	20	65	1/2	35.2	1.3
6	300	20	65	3	32.1	1.2
7	300	20	65	6	31.7	1.2
8	300	20	65	10	30.1	1.2
9	300	20	65	1/4	26.1	1.3

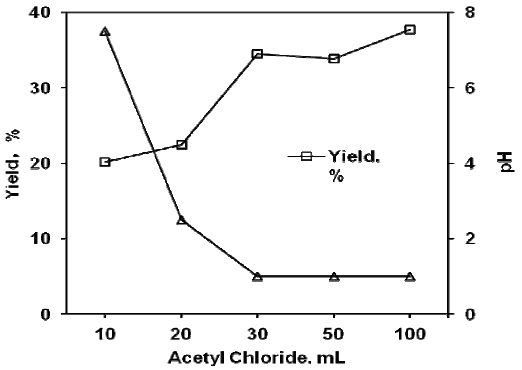


Figure 2: Relationship among the amount of acetyl chloride, yield and pH

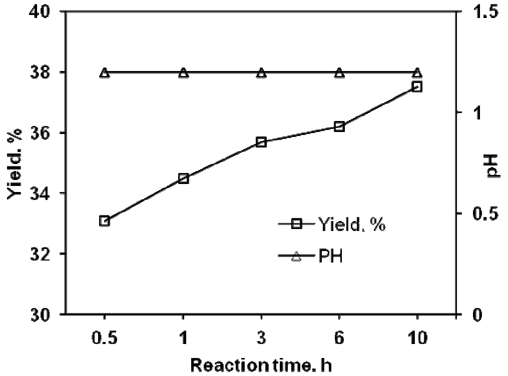


Figure 3: Relationship among reaction time, yield and pH (using AcCl as catalyst)

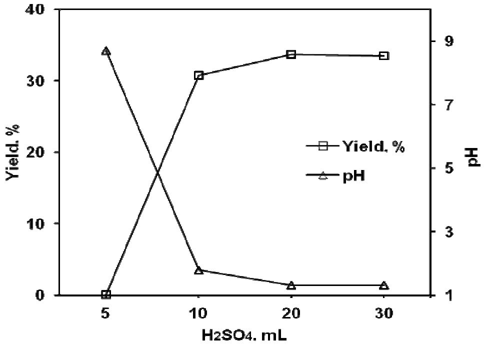


Figure 4: Relationship among the amount of sulfuric acid, yield and pH

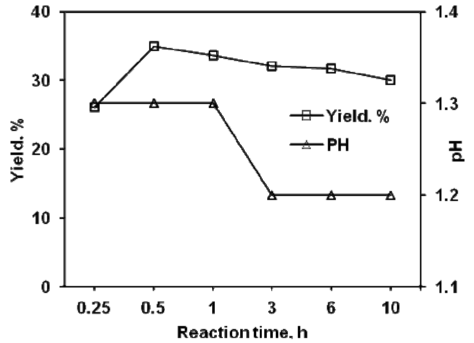


Figure 5: Relationship among reaction time, yield and pH (using sulfuric acid as catalyst)

Therefore, 35% is a reasonable conversion rate for soap skimmings and indicates that the effective components are nearly all converted into biodiesel under the presence of impurities. This result may significantly lower the costs of biodiesel production.

The relationship between the amount of acetyl chloride, biodiesel yield, and pH is shown in Figure 2. The relationship between the reaction time, biodiesel yield, and pH is displayed in Figure 3. As a comparison, the relationship between the amount of sulfuric acid, biodiesel yield, and pH is shown in Figure 4, whereas the relationship between the reaction time, biodiesel yield, and pH is recorded in Figure 5. Overall, the data suggest that the use of a certain amount of acetyl chloride or sulfuric acid is effective for biodiesel production from soap skimmings.

Yield of hemicellulose

The yield of hemicelluloses was low (1.46%), but when soap skimmings are treated for biodiesel production under commercial conditions, a huge amount of hemicelluloses is expected, even with low yield, depending on the amount of soap skimmings treated.

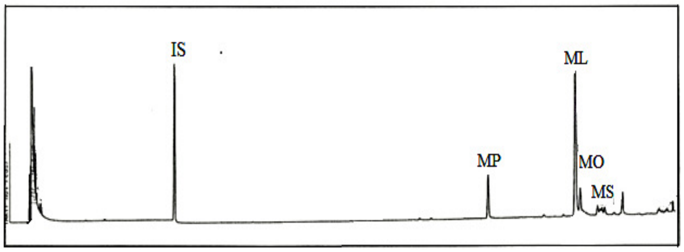
On the other hand, the appearance of the hemicellulose differs depending on the catalyst. Specifically, when acetyl chloride was used as catalyst, the hemicellulose precipitate was grayish in color, and the color could be reduced by washing with methanol. However, when sulfuric acid was used, a whiter precipitate was obtained without washing.

Amount of catalyst (accelerator)

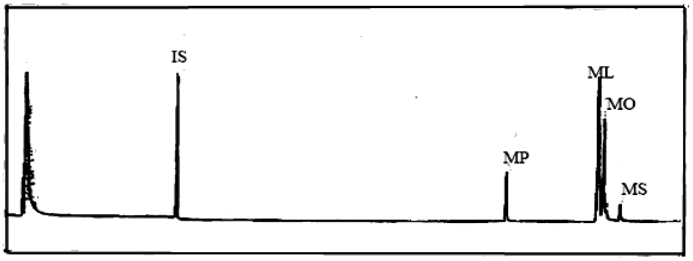
With 150 g of crude tall oil as raw material in the preparation of biodiesel, approximately 10 mL of catalytic acetyl chloride was required in the reaction system.[6] On the other hand, when soap skimmings were used as raw material, 30 mL of acetyl chloride as catalyst was necessary. A similar trend was observed when sulfuric acid was used as catalyst. Specifically, when crude tall oil was used as raw material, 3 mL of sulfuric acid was required,[6] whereas 20 mL was required when soap skimmings were utilized. More acid was required to overcome the basic environment of the soap skimmings and to catalyze the esterification reaction. Because acetyl chloride is a strong Lewis acid, its decomposition in water or alcohol produces acid (e.g., HCl). Therefore, when soap skimmings were used as the raw reaction material, a relatively smaller acetyl chloride increase (10→30 mL, 3 times) was required than for sulfuric acid (3→20 mL, 6.7 times), compared to the case of tall oil.[6]

Reaction time

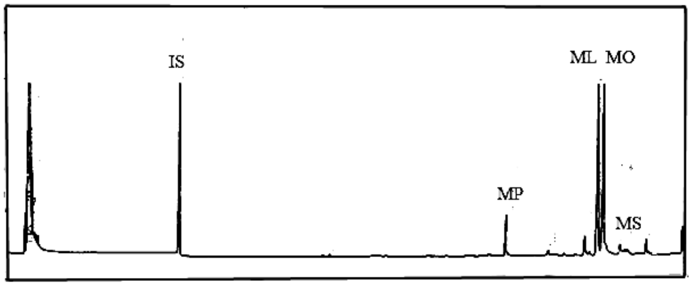
The data trends are shown in Figure 3 and Figure 5. As shown in Figure 3, when acetyl chloride was used as catalyst, the biodiesel yield was 35% after 1 h. Then, for every three additional hours, the rate increased by approximately 1% and then increased by 3% after 10 h. When sulfuric acid was the catalyst, the biodiesel yield was 35% after 0.5-1 h. With longer reaction times, the yield decreased gradually, and after 10 h, the yield decreased by 5%. This decrease was due to the reversible esterification reaction that occurred with the production of water. Because the reaction times had a different effect depending on the catalyst, there is a substantial difference between the two catalysts. However, regardless of the catalyst, a maximum yield of 35% was obtained in approximately 1 h. These results were in contrast with the fact that the acid catalytic esterification reaction is slower than that under alkaline conditions.[7-9] The fatty acids in soap skimmings can be converted into biodiesel, even in their sodium salt forms, but they are not converted under alkaline catalyst. The fatty acids remained in their soap state in the reaction system without conversion. Therefore, this catalytic esterification reaction is completely different from transesterification reactions performed with triglycerides under alkaline conditions.



(1) Biodiesel from soap skimmings (from spruce)



(2) Biodiesel from vegetable oil



(3) Biodiesel from tall oil (from pine)

Figure 6: Gas chromatogram of biodiesel from soap skimmings; IS: internal standard (phenyl ether), MP: methyl palmitate, ML: methyl linoleate, MO: methy oleate, MS: methyl stearate. GC operation conditions: injector temp.: 150 °C, detector temp.: 270 °C, initial temp: 80 °C, Rate: 2 °C/min, max. temp.: 250 °C, column: EC-1, 30 m x 0.25 mm, Alltech Corp.

pH data

Because the raw reaction material is characterized by high moisture content and the presence of a large amount of sodium ions, the pH should have an influence on esterification. Because it is difficult to directly determine the pH of the reaction mixture, the pH of the wash water was tested after the solvent and water phase were separated. The pH of the reaction mixture and the product yield had a close relationship. Specifically, when acetyl chloride was the catalyst (Figure 2), the pH decreased to 1 and the biodiesel yield was near the maximum. Subsequently, regardless of the pH, there was no change in the final yield of the biodiesel. In addition, when 20 mL of concentrated sulfuric acid was used as catalyst, the pH was 1.3 and the biodiesel yield was the highest (Figure 3). No significant changes were observed when more acid was added. The pH of the reaction system and the maximum yield of biodiesel were related because acidic catalysts have two functions: the neutralization of excess base and completion of the esterification reaction.

GC data

The biodiesel product obtained from soap skimmings was tested by GC using the same conditions for biodiesel obtained from vegetable oil and tall oil.[6] The main compositions were similar; the biodiesel was composed of palmitic acid methyl ester (MP), linoleic acid methyl ester (ML), methyl oleate (MO), and methyl stearate (MS). This result suggests that the fatty acids in plants can be quantitatively converted to the corresponding fatty acid esters, despite the presence of salt and other impurities. The chromatogram is shown in Fig. 6.

Biodiesel characterization

For comparison with commercial diesel, the density, viscosity, and heat of combustion were measured, and the recorded data are presented in Table 3 and Table 4. The biodiesel showed a slightly lower performance than commercial diesel, indicating that the biodiesel obtained by this method should be mixed with commercial diesel for use. In addition, it is possible to independently use the biodiesel obtained by this method as an energy source in diesel engines and boilers. However, this is a first attempt at biodiesel production from soap skimmings and it has been focused more on the production process from non-food-related raw materials. Therefore, the experiment was limited only to items available in our lab. In the future, the ASTM property test will be required for practical use. The biodiesel from vegetable oil is a sound representative, but it is too early to judge the long-term effectiveness. The properties of each biodiesel may have some differences depending on the source materials. The supply of vegetable oil is limited beyond waste vegetable oil. Multiple types of biodiesels and sources should be established. For example, a process that involved the simultaneous catalytic hydrogenation and cracking was applied to tall oil and different types of biodiesel were produced by Liu *et al.*[10] The contaminants of biodiesel are different depending on the source materials and method used to obtain it. Therefore, we are looking for raw materials outside the food supply chain, using the boiling point (b.p.) and GC chromatograms as parameters. Biodiesel requires some acceptable range of properties because of the different raw materials and methods applied.

Table 3
Comparison on density and viscosity of biodiesels

Test#	Temp. (ºC)	ρ (g/cm^3)	μ (cm^2/s)
D-3	30	0.914	10.91
D-5	30	0.924	8.46
D-13	30	0.879	10.14
D-14	30	0.934	9.51
D-V1*	30	0.926	10.28
D-V2*	30	0.905	6.87
D-C*	30	0.880	7.98

*D-V1, V2: vegetable oil converted to biodiesel, 1: using acetyl chloride, 2: using sulfuric acid; *d-c: commercial diesel

Table 4
Comparison on heat of combustion

Test#	Fuel consumed (g)	Heat of combustion (HHV), BTU/Ib	Average heat of combustion, BTU/Ib
D-5	0.358	19618	19559
D-5	0.360	19509	
D-14	0.362	19401	19375
D-14	0.363	19348	
D-C*	0.357	19673$^{\Delta}$	19673
D-C*	0.357	19673$^{\Delta}$	

*D-C: commercial diesel; Δ: data source: petroleum-based fuels property database, NREL (http://www.nrel.gov/vehiclesandfuels/apbf/progs/search1.cgi)

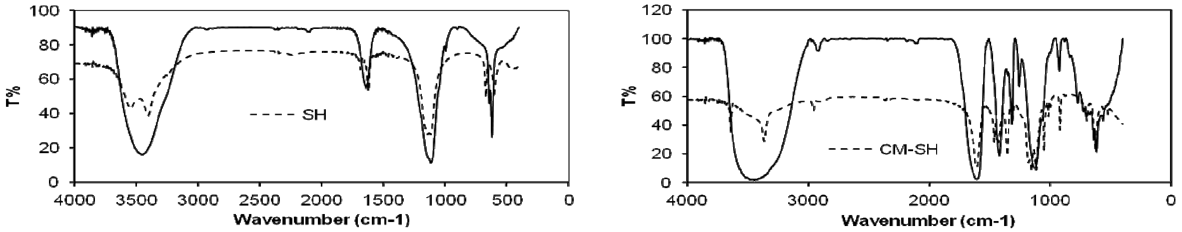


Figure 7: FT-IR spectra of hemicelluloses and CM-hemicelluloses

Table 5
Molecular weights of CM-hemicelluloses

Sample	Mw	Mn	Polydispersity
CM-soap skim. H.	31860 (26500)	30897 (23700)	1.03 (1.12)
CM-wheat straw H.	1810 (608)	1565 (577)	1.16 (1.05)
CM-com. xylan	3504	3414	1.03

FT-IR of separated hemicellulose

The FT-IR spectra of the separated hemicellulosic components and the CM-products are shown in Fig. 7. The hemicellulose from soap skimmings exhibited the expected pattern for hemicellulosic moieties, and the IR spectra were slightly different from the IR spectra of wheat straw xylan from black liquor.[11] The signals in the 3600-2800 cm^{-1} region are due to the stretching vibrations of CH and OH. However, one is split into two broad bands, and the other is a single broad band. The C-O stretching region (1200-950 cm^{-1}) is also visible. A sharp band at approximately 1110 cm^{-1} is due to the typical absorption of xylans, indicating dominant xylan in the isolated hemicellulose. Another sharp band was observed at 1639 cm^{-1}, indicating the presence of uronic acid in the hemicellulose. The sharp band at 618 cm^{-1} is the characteristic absorption peak of a five-carbon ring. When compared with ordinary hemicellulose, the IR spectra of CMH show an additional strong absorption at 1601 cm^{-1}, confirming the presence of COO^- groups.[12] The strong absorption peaks observed at 1314 and 1417 cm^{-1} were assigned to $–CH_2$ scissoring and –OH bending vibrations, respectively. Additionally, a new peak was observed near 2950 cm^{-1} and could be assigned to the $–CH_2$ groups derived from the carboxymethyl group ($-H_2COOH$). These results indicated that carboxymethyl groups were successfully introduced into the product. In the fingerprint range, the difference between CM-SH and CM-wheat straw H could be observed more clearly. The original SH and wheat straw H looked similar, but they were actually different and had a similar xylose main chain. The differences in the IR spectra were also supported by the CM-IR spectra and molecular weight data of the CM sample. Therefore, SH and wheat straw H have the same xylose chains, but the molecular weights are significantly different. Therefore, the effect of blanches is relatively small in the IR spectra.

Molecular weight of carboxymethylated hemicellulose (CMH)

The molecular weight of CMH from soap skimmings is much larger than the CM-wheat straw hemicellulose and CM-commercial softwood xylan (Table 5). Only a part of the large molecular weight fraction may be solidified in alkaline Kraft pulp black liquor in the soap skimming process. In general, hemicellulose is precipitated under acidic conditions, but soap skimmings are produced under alkali conditions. In other words, the solidified hemicelluloses in the soap skimmings can be considered the high molecular fraction in the Kraft pulp black liquor.

SEM

The SEM images shown in Fig. 8 indicate that the hemicellulose consisted of larger particles, whereas those of the CMH were much finer. The images show the macromolecular structure of the carboxymethylated samples resulting from the –CH_2COOH group. There was no significant difference between the hemicellulose from the soda cooking black liquor of wheat straw and from soap skimmings.[11]

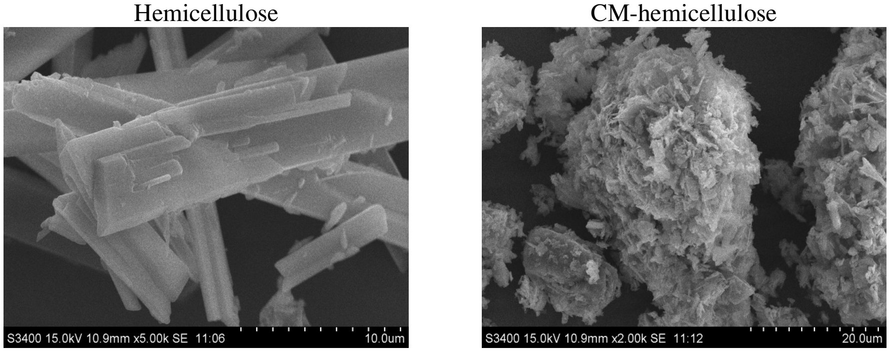

Hemicellulose
CM-hemicellulose

Figure 8: SEM photos of hemicelluloses and CM-hemicelluloses from soap skimmings

CONCLUSION

The results revealed that either acetyl chloride or concentrated sulfuric acid could be used as a catalyst. The biodiesel yield was 35% when the amounts of acetyl chloride and sulfuric acid were 30 mL and 20 mL (for 150 g of soap skimmings), respectively. Simultaneously, some hemicellulosic components could be obtained during the separation process of biodiesel. This study has practical significance for industrial applications of soap skimmings and in reducing the cost of biodiesel. The hemicellulose separated during biodiesel production process could also be useful for the selective collection of high molecular weight species.

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