

# Homogeneous Derivatization of Sugarcane Bagasse with Myristyl Chloride at Room Temperature to Prepare Bio-based Oil Absorbents

Aiping Zhang,<sup>a</sup> Chuanfu Liu,<sup>b,\*</sup> Jun Xie,<sup>a</sup> and Runcang Sun<sup>b,c</sup>

Homogeneous myristoylation of sugarcane bagasse (SCB) was investigated at room temperature in dimethyl sulfoxide/*N*-methylimidazole (DMSO/NMI) without any additional catalysts. The effects of reaction time and the dosage of myristyl chloride on the extent of myristoylation were studied. The weight percent gain (WPG) of the modified SCB was 10.7 to 133.2%. The role of NMI as solvent, base, and catalyst at room temperature was proposed. FT-IR and solid-state CP/MAS <sup>13</sup>C-NMR analyses provided evidence of myristoylation. The reactions of carbohydrate and lignin fractions were both confirmed. Solid-state CP/MAS <sup>13</sup>C-NMR also implied the reaction of three hydroxyl groups at C-2, C-3, and C-6 positions in cellulose. The modified SCB could easily absorb oil with the capacity of 1.57 to 3.76 g/g for engine oil and 1.72 to 3.55 g/g for vacuum pump oil. The enhanced oil capacities exhibited similar trends in terms of WPG with increased reaction parameters. This modified SCB can be used as a potential oil absorbent.

*Keywords:* Oil absorbent; Sugarcane bagasse; Homogeneous modification; Room temperature; Myristyl chloride; Dimethyl sulfoxide/*N*-methylimidazole

*Contact information:* a: Institute of New Energy and New Material/Guangdong Key Laboratory for Innovative Development and Utilization of Forest Plant Germplasm, South China Agricultural University, Guangzhou 510642, China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China; c: Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, China; \* Corresponding author: chfliu@scut.edu.cn

## INTRODUCTION

In recent years, there have been worldwide pollution problems caused by accidental and intentional oil discharges during the production, transportation, and refining of petroleum (Solisio *et al.* 2002; Sokker *et al.* 2011). The spilled oil must be removed from either land or water to avoid immense environmental damage. One of the most effective, efficient, and economical methods for the oil cleanup is the use of oil absorbents based on their hydrophobic and lipophilic characteristics (Sokker *et al.* 2011). However, commercial synthetic oil absorbents are environmentally undesirable due to their non-biodegradability or very slow biodegradability. The readily available, biodegradable, and renewable lignocelluloses have potential as oil absorbents, especially after the attachment of hydrophobic groups to increase the lipophilicity and decrease the hydrophilicity.

Lignocelluloses are inhomogeneous complex biopolymers composed of three main components including cellulose, hemicelluloses, and lignin (Gellerstedt and Gatenholm 1999; Mohanty *et al.* 2000). Hydroxyl groups are the most abundant and reactive sites susceptible to chemical reaction in lignocelluloses and other biopolymers,

providing the potential to prepare novel functional composites by the attachment of a variety of functional groups.

A series of functional products have been extensively prepared by etherification, esterification, graft co-polymerization, crosslinking, oxidation, and other derivatization of hydroxyl groups. For example, modification of starch (Kweon *et al.* 2001) and cellulose (Yoshimura *et al.* 2006) with succinic anhydride imparted the increased hydrophilic properties to the biopolymers. Similarly, the replacement of hydroxyls with hydrophobic benzoyl (Evans *et al.* 2002) and acetyl (Sun *et al.* 2003) groups could enhance the lipophilic properties as well as the compatibility with thermoplastics.

Compared with a heterogeneous reaction, homogeneous reactions are simple, easily controllable, and highly reproducible. Because of the complexity of whole cell walls, lignocellulose is insoluble in water and most organic solvents, and this constitutes a major obstacle for its modification and utilization. The heterogeneous reaction of lignocelluloses generally occurs on the surface, and the reaction of the inaccessible hydroxyl groups depends heavily on the penetration of reagents into the interior of cell walls.

Due to unavailability of effective solvents of lignocelluloses, most studies have to focus on heterogeneous modification (Ren *et al.* 2008; Kamel *et al.* 2012) of the whole lignocelluloses and the homogeneous modification (Schlufter *et al.* 2006; Cao *et al.* 2009) of the isolated components. Homogeneous derivatization of lignocelluloses was believed to be impossible until the development of novel solvent systems for lignocelluloses including dimethyl sulfoxide/*N*-methylimidazole (DMSO/NMI, 2:1, v/v) (Lu and Ralph 2003), ionic liquids (ILs) (Kilpelainen *et al.* 2007; Xie *et al.* 2007), and DMSO/lithium chloride (LiCl) (Wang *et al.* 2009) in the past decade. Much effort has been devoted to the derivatization of lignocelluloses in ionic liquids due to their unique properties (Xie *et al.* 2007; Yuan *et al.* 2010, 2011; Chen *et al.* 2013). However, the dissolution and subsequent derivatization of lignocelluloses in ionic liquids require relatively high temperature, which easily leads to the degradation of the biopolymers. As an alternative, the solvent system DMSO/NMI (2:1, v/v) (Lu and Ralph 2003) and DMSO/LiCl (Wang *et al.* 2009) can readily dissolve the whole cell wall without any degradation at low temperature, providing the novel utilization of lignocellulose. Lignocellulosic biomass film was first prepared directly from bagasse solution in DMSO/LiCl (Chen *et al.* 2014). The homogeneous succinylation, benzoylation, and palmitoylation of eucalyptus wood (Zhang *et al.* 2012; Zhang *et al.* 2013) was also achieved at room temperature in DMSO/NMI without any additional catalysts. However, due to the limited content of the attached hydrophobic groups, the benzoylated (Zhang *et al.* 2012) and palmitoylated wood (Zhang *et al.* 2013) with relatively low weight percent gain (WPG) did not exhibit satisfactory oil absorption. Commonly, the reactivity of aliphatic acid chlorides with polysaccharides at high temperature increases with the decreasing chain length.

To prepare bio-based oil absorbents, a long chain fatty acid chloride, myristyl chloride, was selected in the present study to improve the reactivity of ball-milled sugarcane bagasse (SCB) at room temperature in DMSO/NMI and to attach a long-chain lipophilic group onto SCB. The chemical structure of modified SCB was characterized with FT-IR and solid-state <sup>13</sup>C-NMR spectroscopy. The oil absorptivity was also examined using engine oil and vacuum pump oil to explore the possibility of the derivatized SCB as an oil absorbent.

## EXPERIMENTAL

### Materials and Chemicals

Sugarcane bagasse (SCB) was kindly provided by Guangxi Guitang (Group) Co., Ltd. (Guigang, China). It was dried at 60 °C in an oven for 72 h, ground, and screened to prepare 20 to 60 mesh size particles. The dried ground samples were extracted with toluene-ethanol (2:1, v/v) in a Soxhlet extractor for 12 h and milled in a planetary ball mill for 36 h. The dewaxed and ball-milled SCB contained 47.12% cellulose, 33.13% hemicelluloses, 19.24% lignin, and 0.51% ash.

Myristyl chloride, DMSO, and NMI were purchased from Aladdin Reagent Co. (Shanghai, China). Engine oil and vacuum pump oil were supplied by Yushao Trading Co., Ltd. (Guangzhou, China). Others chemicals were obtained from Guangzhou Chemical Reagent Factory (Guangdong, China). All chemicals were of analytical grade and directly used as received without further purification.

### Homogeneous Modification of SCB at Room Temperature

The homogeneous myristoylation of SCB was carried out at room temperature in DMSO/NMI (2:1, v/v) solvent system under the conditions in Table 1. Ball-milled SCB (300 mg) was suspended in 6 mL of DMSO and 3 mL of NMI with magnetic agitation at room temperature for 5 h to guarantee the complete dissolution of SCB, which was confirmed with the dark-field illumination of a polarizing light microscope. Myristyl chloride was carefully added portionwise into the SCB solution, and the mixture was stirred at room temperature for myristoylation. After the required time, the mixture was slowly poured into 100 mL of isopropanol with agitation to precipitate the modified SCB. The resulting suspension was further stirred for 30 min, and the solid residues were filtered out with 0.2 µm of membrane. The residues was washed thrice with 100 mL isopropanol to eliminate DMSO, NMI, unreacted reagent, and byproducts, and freeze-dried to obtain SCB derivatives. WPG of the SCB derivatives was calculated according to the following equation,

$$\text{WPG}=(M_1-M_0)/M_0\times 100\% \quad (1)$$

where  $M_0$  and  $M_1$  are the dry weights of the SCB before and after modification, respectively.

### Characterization of Unmodified and Myristoylated SCB

FT-IR spectra of the unmodified and myristoylated SCB were recorded on an FT-IR spectrophotometer (Tensor 27, Bruker, Germany) from finely ground samples (1%, w/w) in KBr pellets in the range of 4000 to 400  $\text{cm}^{-1}$ . Thirty-two scans were taken for each sample with a resolution of 2  $\text{cm}^{-1}$  in the transmittance mode.

The solid-state  $^{13}\text{C}$ -NMR spectra were obtained on a Bruker DRX-400 spectrometer (Germany) at 100 MHz with a 5 mm MAS BBO probe employing both cross polarization (CP) and magic angle spinning (MAS) at ambient temperature. The detailed collecting and processing parameters were as follows: number of scans 1845, receiver gain 64, acquisition time 0.013 s, relaxation delay 2.0 s, pulse width 3.2986 s, spectrometer frequency 100.61 MHz, spectral width 29761.9 Hz, acquired size 384, and spectral size 1024.

## Oil Absorption

The SCB sample (100 mg) was suspended in 1.5 mL of oil in a centrifugal tube. The suspension was shaken for 1 h in a MaxQ4450 Benchtop Orbital Incubated Shaker at 25°C with shaking speed of 200 rpm, and centrifuged at 10000 rpm for 15 min. The whole centrifugal tube was put the bottom up to remove the liquids and collect the solid residues. The oil absorptivity of the sample was calculated using Eq. 2,

$$\text{Oil absorptivity} = (W_1 - W_0) / W_0 \times 100\% \quad (2)$$

where  $W_0$  and  $W_1$  are the weights of the sample before and after the oil absorption, respectively.

## RESULTS AND DISCUSSION

### Homogeneous Myristoylated of SCB at Room Temperature

The homogeneous modification of SCB with myristyl chloride was investigated in the present study in DMSO/NMI at room temperature without any additional catalysts. The effects of the reaction time and the weight ratio of myristyl chloride to SCB on the WPG of the modified SCB were evaluated, and the results are listed in Table 1.

**Table 1.** WPG of the Modified SCB with Myristyl Chloride at Room Temperature in DMSO/NMI and Their Oil Absorptivity

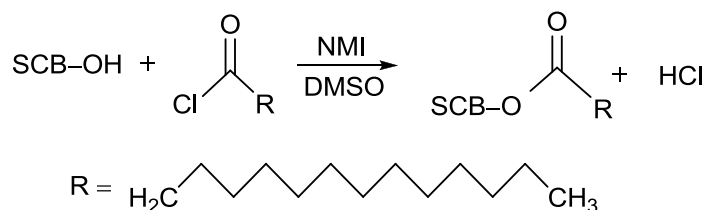
Modification conditions		Samples No	WPG (%)	Hydroxyls substituted <sup>b</sup> (mmol/g)	Oil absorptivity (g/g)	
Weight ratio <sup>a</sup> (g/g)	Reaction time (h)				Engine oil	Vacuum pump oil
/	/	Control	/	/	0.93	0.86
1:1	3.0	1	10.7	0.51	1.57	1.72
2:1	3.0	2	33.9	1.61	2.24	2.18
3:1	3.0	3	70.4	3.35	3.14	2.86
4:1	3.0	4	95.0	4.52	3.38	3.21
5:1	3.0	5	108.4	5.16	3.51	3.44
6:1	3.0	6	133.2	6.34	3.74	3.55
3:1	0.25	7	28.4	1.35	1.87	1.92
3:1	0.5	8	43.2	2.06	2.68	2.50
3:1	0.75	9	71.6	3.41	3.25	3.05
3:1	1.0	10	73.5	3.50	3.39	3.24
3:1	2.0	11	70.9	3.37	3.16	3.04
3:1	4.0	12	59.8	2.85	3.03	2.78

<sup>a</sup> Weight ratio of the myristyl chloride to dried SCB (g/g).

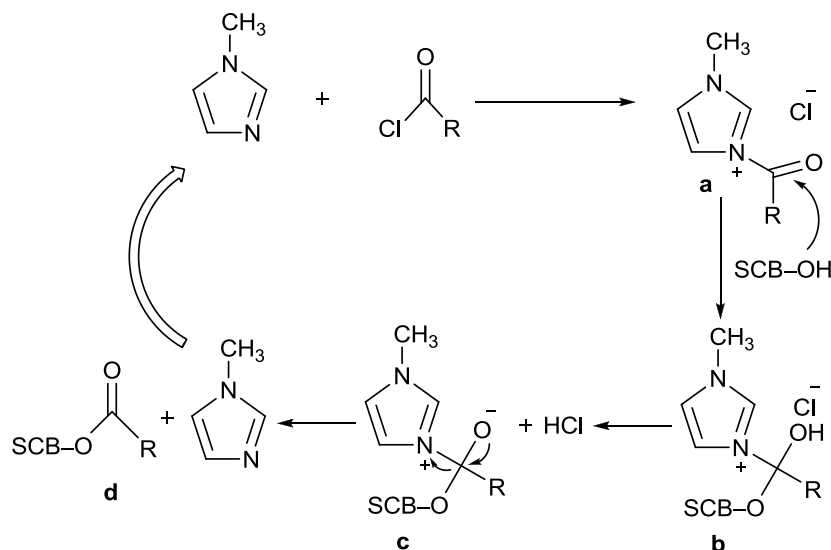
<sup>b</sup> Hydroxyl groups substituted, calculated from WPG (mmol/g).

As shown in Table 1, when keeping the reaction time at 3.0 h, an increase of the weight ratio of myristyl chloride to SCB from 1:1 to 2:1, 3:1, 4:1, 5:1, and 6:1 resulted in an increase in WPG from 10.7% to 33.9%, 70.4%, 95.0%, 108.4%, and 133.2%, respectively, indicating the achievement of SCB modification at room temperature in DMSO/NMI. This positive effect could be due to the greater availability of myristyl chloride in the proximity of the reactive hydroxyl groups at a higher weight ratio of myristyl chloride to SCB. Hydroxyl groups are the main functional groups and reaction sites on SCB. Actually, the reaction between SCB and myristyl chloride is the reaction of

the reactive hydroxyl groups in SCB with chloride as shown in Fig. 1, resulting in the attachment of myristoyl group onto SCB and the byproduct hydrochloric acid (HCl). Commonly, compared with short chain aliphatic acid anhydrides and chlorides, the reactions of long chain aliphatic acid chlorides with polysaccharides occur at relatively high temperature, because of their decreased reactivity with the increased chain length. The unexpectedly easily achieved homogeneous modification of lignocellulose at room temperature was probably due to the special structure of NMI. The imidazole-derived heterocyclic compound NMI contains two basic nitrogen atoms, providing more support for the modification at room temperature. The possible mechanism of NMI for the myristoylation is illustrated in Fig. 2. NMI reacts with myristyl chloride to form an intermediate due to the attack of the nucleophilic nitrogen in NMI to the electron-deficient carbon of carbonyl group in myristyl chloride. This intermediate can more easily attack hydroxyl groups in SCB than myristyl chloride to form intermediate b. Due to the basicity of nitrogen in NMI, intermediate b deprotonates to form byproduct HCl and intermediate c. Meanwhile, because of the tendency of hydroxyl oxygen to link with carbonyl group at the presence of electron-sufficient oxygen, intermediate c can easily cleave to modified SCB and NMI. NMI enters into the next cycle of catalyzed myristoylation to perform SCB modification. Therefore, the role of NMI in the modification is not only a solvent, but also a base and a catalyst.



**Fig. 1.** Homogeneous reaction between SCB and myristyl chloride in DMSO/NMI at room temperature without any additional catalysts



**Fig. 2.** Possible mechanism of myristoylation reaction of SCB with myristyl chloride in DMSO/NMI at room temperature

Holding the weight ratio of myristyl chloride to SCB at 3:1, the WPG reached 28.4% in 0.25 h, 43.2% in 0.5 h, 71.6% within 0.75 h, and 73.5% within 1.0 h, indicating a favorable effect of reaction time on myristoylation due to the increased molecular collision at the prolonged duration. However, further increase of reaction time from 1.0 to 2.0, 3.0, and 4.0 h led to a decrease in WPG from 73.5% to 70.9%, 70.4%, and 59.8%, respectively, which was probably due to the increased degradation and hydrolysis of the modified SCB with the formation of the acidic byproduct HCl.

The WPG of the modified SCB was 10.7 to 133.2% under the selected conditions, corresponding to 0.51 to 6.34 mmol/g hydroxyl groups substituted in SCB at room temperature in DMSO/NMI, as shown in Table 1. These values of hydroxyl groups substituted in myristoylation were much higher than those in palmitoylation (0.37 to 1.93 mmol/g) (Zhang *et al.* 2013), which was probably due to the lower chain length of myristoyl chloride compared with palmitoyl chloride. Comparatively, the modification of spruce wood with lauroyl chloride in IL 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl) with pyridine as a catalyst resulted in 12.58 mmol/g hydroxyl groups substituted (Xie *et al.* 2009), while the modification of poplar wood in [C<sub>4</sub>mim]Cl with triethylamine as a catalyst at 80 °C led to much more hydroxyl groups substituted (11.1-35.4 mmol/g) (Yuan *et al.* 2011). The catalysis of pyridine and triethylamine at high temperature was probably responsible for the high values of hydroxyl groups substituted. The decreased chain length of lauroyl chloride may be another reason. In the present study, considering that the modification of SCB was performed at room temperature without any additional catalysts, the relatively low level of substitution of hydroxyl groups (0.51 to 6.34 mmol/g) was reasonable and acceptable. Similarly, 13.75 mmol/g hydroxyl groups was substituted in wood benzylation with pyridine as a catalyst in [C<sub>4</sub>mim]Cl (Xie *et al.* 2007, 2009), while only 4.14 mmol/g hydroxyl groups was substituted at room temperature in DMSO/NMI (Zhang *et al.* 2012). In addition, the dissolution and derivatization of biopolymers may decrease over 30% of their starting DP in ILs (Heinze *et al.* 2005; Liu *et al.* 2006; El Seoud *et al.* 2007). Therefore, DMSO/NMI system may be a good choice due to the easy achievement of the highly efficient derivatization and the decreased demand on energies and equipment for the dissolution and derivatization of lignocelluloses.

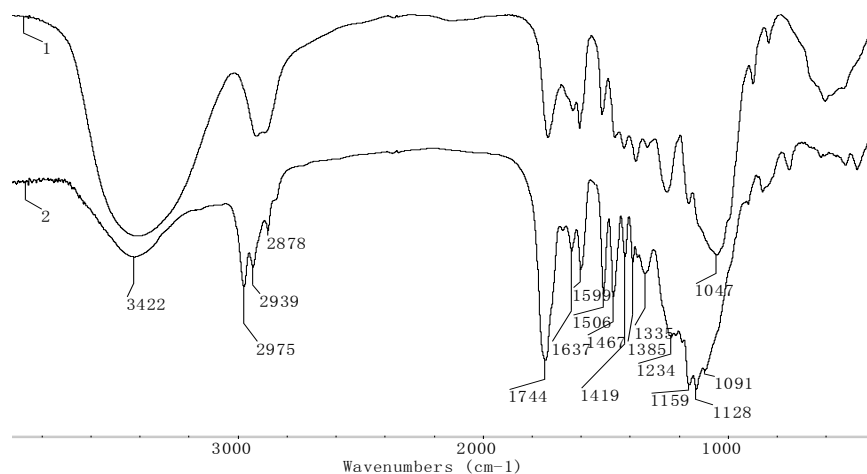
### FT-IR Spectra

Figure 3 illustrates the FT-IR spectra of ball-milled SCB (spectrum 1) and myristoylated SCB sample 10 (spectrum 2). Compared with that of ball-milled SCB, the changes of the characteristic bands in spectrum 2 of modified SCB provide evidence of myristoylation. The intensities of the bands for C-H stretching of aliphatic groups (2975, 2939, and 2878 cm<sup>-1</sup>), C=O stretching in ester (1744 cm<sup>-1</sup>), C-H bending (1467 cm<sup>-1</sup>), and C-O stretching in ester (1234 and 1159-1091 cm<sup>-1</sup> for anti-symmetric and symmetric stretching, respectively) (Yoshimura *et al.* 2006) were significantly increased after derivatization. These changes indicated the attachment of acyl group with long chain aliphatic onto SCB, which confirmed the occurrence of myristoylation in Fig. 1.

### Solid-State CP/MAS <sup>13</sup>C-NMR Spectra

Solid-state CP/MAS <sup>13</sup>C-NMR spectroscopy is the most effective method to directly provide the detailed structural information of the solid samples. Figure 4 illustrates the solid-state CP/MAS <sup>13</sup>C-NMR spectra of ball-milled SCB (A) and myristoylated SCB sample 10 (B). In general, the carbon signals of lignocelluloses are

distributed in four ranges in the solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra (Chang and Chang 2001; Maunu 2002): 180-160 ppm for carbonyl carbons, 160-110 ppm for aromatic carbons, 110-50 ppm for carbohydrate carbons, and 50-10 ppm for aliphatic carbons. In spectrum A, the primary signals are specific for the carbons from native SCB. The small signals at 172.2 and 21.0 ppm are attributed to carbonyl and methyl carbons, respectively, of acetyl groups in hemicelluloses. The signal at 55.9 ppm is associated with the methoxy group in lignin. Due to the low resolution of aromatic carbon signals of lignin in the solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra, only several minor overlapped signals were observed at 135.7, 147.5, and 152.8 ppm, which are originated from C-1, C-3, and C-4 of lignin syringyl and guaiacyl units (Lu and Ralph 2003), respectively. More importantly, the strong signals at 103.8 (C-1 of cellulose and xylan), 82.4 (C-4 of amorphous cellulose), 74.5 (C-2, C-3, and C-5 of cellulose; C-2, C-3, and C-4 of xylan), and 61.4 ppm (C-6 of cellulose and C-5 of xylan) from polysaccharides were all observed in carbohydrate carbon range. The primary signals for C-4 at amorphous cellulose suggested that the crystalline structure of native cellulose was extensively destroyed after ball-milling for 36 h, which was favorable for the dissolution of SCB.

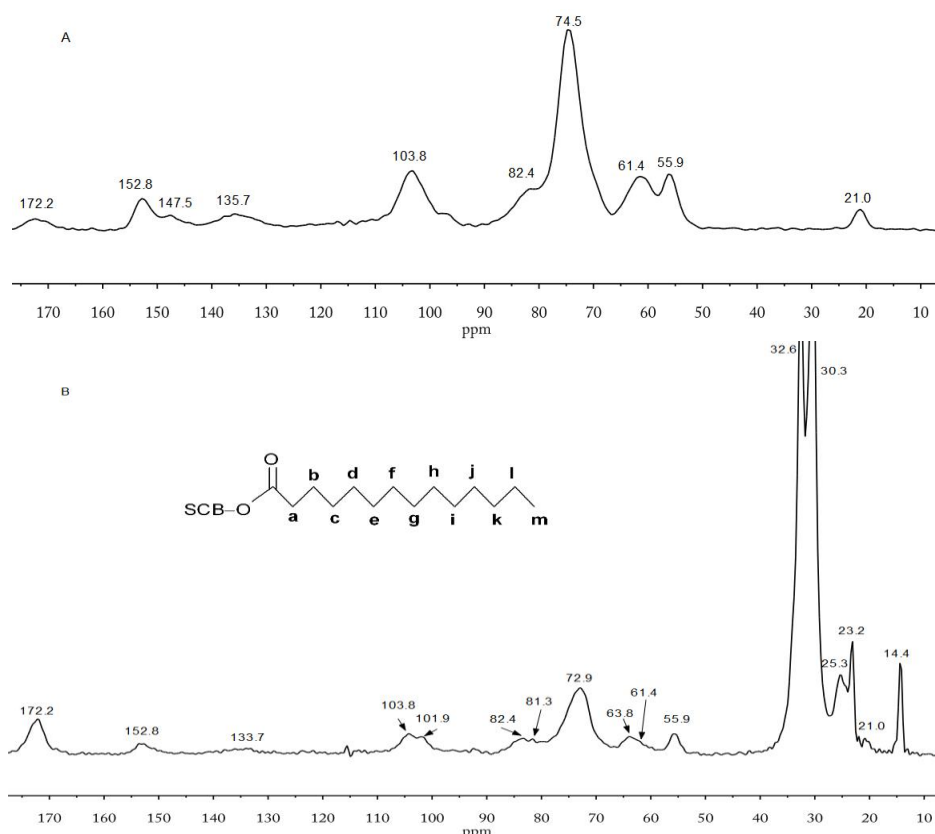


**Fig. 3.** FT-IR spectra of ball-milled bagasse (spectrum 1) and myristoylated SCB sample 10 (spectrum 2)

Comparatively, the intensity of the carbonyl carbon signal at 172.2 ppm was significantly increased after myristoylation, suggesting the attachment of acyl group onto SCB. In the aliphatic carbon range, the new strong signals at 14.4 (methyl carbon in the end, m position of myristoyl group), 23.2 (methylene carbon, l position), 25.3 (methylene carbon, b position), 32.6 (methylene carbons, a and k positions), and 30.3 ppm (methylene carbons, other positions from c to j) indicated the attachment of long chain aliphatics onto SCB. These changes implied the myristoylation reaction in Fig. 1 occurred, corresponding to the results from FT-IR analysis.

In the carbohydrate carbon range, the strong signal at 74.5 ppm in ball-milled SCB was shifted to 72.9 ppm in myristoylated SCB, indicating the reaction of hydroxyl groups at C-2 and C-3 positions of cellulose and xylan. The signals for C-6 of cellulose and C-5 of xylan were separated to a shoulder at 61.4 ppm and a band at 63.8 ppm. The former shoulder arises from C-5 of xylan and the un-substituted C-6 of cellulose, and the latter band relates to the substituted C-6 of cellulose (Miyamoto *et al.* 1984; Sei *et al.* 1985). This change indicated the occurrence of the reaction of hydroxyl groups at the

cellulose C-6 position. In addition, the signal for C-1 of cellulose and xylan was split to two signals at 103.8 and 101.9 ppm. The new emerged signal at 101.9 ppm is assigned to C-1 of cellulose and xylan with adjacent substituted C-2 (Miyamoto *et al.* 1984; Sei *et al.* 1985). Similarly, the signal for C-4 of cellulose was split to the original unsubstituted C-4 signal at 82.4 ppm and the C-4 signal with adjacent substituted C-3 (Miyamoto *et al.* 1984; Sei *et al.* 1985). These split C-1 and C-4 signals indicated that the derivatization of the hydroxyl groups at C-2 and C-3 positions does occur.



**Fig. 4.** Solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra of ball-milled bagasse (A) and myristoylated SCB sample 10 (B)

In the aromatic carbon range, the signals from lignin fraction was slightly influenced by modification, and the weak signal at 135.7 in ball-milled SCB was shifted to 133.7 ppm in modified SCB, and that at 147.5 ppm was also shifted to 145.6 ppm (not shown due to the high contour). These changes revealed the occurrence of the myristoylation on lignin fractions.

Based on the comparative analysis of solid-state CP/MAS  $^{13}\text{C}$ -NMR spectra of ball-milled SCB and myristoylated SCB, the reaction in Fig. 1 on the three main components does occur. The myristoylation reactions of three hydroxyl groups at C-2, C-3, and C-6 positions in cellulose all were confirmed.

### Oil Absorptivity

The oil absorption of ball-milled unmodified SCB and myristoylated SCB was comparatively examined using engine oil and vacuum pump oil, respectively, and the results are summarized in Table 1. Because of the attachment of hydrophobic myristoyl



group, the capacity of engine oil increased from 0.93 g/g ball-milled SCB to 1.57-3.76 g/g modified SCB, and that of vacuum pump oil increased from 0.86 g/g of ball-milled SCB to 1.72-3.55 g/g of modified SCB. The increased absorptivity for engine oil and vacuum pump oil also exhibited similar trends as WPG with the increased reaction time and the dosage of myristyl chloride under the selected conditions, which indicated that the attached hydrophobic myristoyl group was responsible for the increased oil capacity. It should be mentioned that to reduce the error and confirm the results, the oil absorbed on the samples was calculated after centrifugation at 10000 rpm for 15 min to retain only the tightly absorbed oil. The oil capacities absorbed on the myristoylated SCB were much higher than the tightly absorbed oil obtained in our laboratory due to the characteristic of physical absorption. Therefore, the myristoylated SCB can be used as a potential oil absorbent in oil spill cleanup.

## CONCLUSIONS

1. Homogeneous modification of SCB with myristyl chloride was accomplished at room temperature in DMSO/NMI. The effects of reaction time and weight ratio of myristyl chloride to SCB on WPG were investigated, and WPG ranged from 10.7% to 133.2% under the selected conditions.
2. The role of NMI and its possible mechanism were elucidated in the myristoylation at room temperature in DMSO/NMI.
3. FT-IR and CP/MAS  $^{13}\text{C}$ -NMR analyses revealed the occurrence of myristoylation on carbohydrate and lignin fractions. The reaction of three hydroxyl groups at C-2, C-3, and C-6 positions in cellulose was all confirmed.
4. The increased oil capacities of the myristoylated SCB were 1.57 to 3.76 g/g for engine oil and 1.72 to 3.55 g/g for vacuum pump oil, exhibiting the trends similar as WPG with the increased reaction parameters. This myristoylated SCB can be used as a potential oil absorbent in oil spill cleanup.

## ACKNOWLEDGEMENTS

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