

Chapter 8

**REPRODUCIBILITY OF NATURAL
RESOURCES FOR THE SYNTHESIS OF LOW
TRANSITION TEMPERATURE
MIXTURES (LTTMs)**

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ABSTRACT

LTTMs are combinations of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs) as a new class of green solvents which aim to overcome the limitation of ionic liquids while sharing some of their advantages. The materials used as HBDs were malic acids extracted from cactus, papaya, and luffa cylindrica while HBAs were L-proline, L-histidine, glycine, and choline chloride, all of which existed naturally in

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living organisms or plants. Compatibility of different combinations of HBD and HBA to form LTTMs and varying their molar ratio were the subjects of interest in this project. A biopolymer solubility test was carried out on all LTTMs to identify the best performed LTTM and utilize it in oil palm empty fruit bunch biomass pretreatment. For LTTMs synthesis, only histidine was incompatible with malic acid. The solubility screening test showed that combination of cactus and proline with a molar ratio of 1:1 (CP 1:1) is the most effective LTTM in dissolving lignin (12.87 wt%), followed by luffa cylindrica : proline 1:1 (11.53 wt%). FTIR analysis was carried out and proved the existence and formation of a hydrogen bond within the solvent structure. The most critical disadvantage of LTTMs was the thermal instability due to its weak hydrogen bonding. CP 1:1 showed the similar result in biomass pretreatment to the biopolymers solubility screening test, which is around 12 wt% of lignin solubility. This work provides an alternative method of biomass pretreatment for lignin extraction.

Keywords: low transition temperature mixtures, hydrogen bond donor, hydrogen bond acceptor, compatibility

INTRODUCTION

In recent decades, researchers have been putting a lot of focus on renewable energy sources, for example, solar, wind, geothermal and biomass energy. Biomass is one of the most abundant natural resources where its potential has yet to be fully discovered and utilized. Lignocellulose is the major component of biomass, which is composed of three types of biopolymers: lignin, cellulose, and hemicellulose (Lee et al. 2009, Pérez et al. 2002). Lignocellulosic biomass of oil palm contains 18-35% lignin content, 40 - 50% cellulose, and 20-40% hemicellulose (Sun et al. 2011). Nevertheless, lignocellulosic biomass is highly recalcitrant to biotransformation (Lee et al. 2009), hence there are limited types of solvents which can be used to dissolve biopolymers and the polymer properties are not modifiable. In this context, efficient separation technologies and processes are needed to extract these components for researches and synthesis of value-added biomass products or as fuel.

Since the introduction of the concept ‘green chemistry’, the newly proposed processes or methodologies have been incorporated with environmental consideration. However, lignocellulosic biomass processing using ionic liquids (ILs) is not yet being commercialized. There are obstacles that needed to be tackled in order for ILs to be applied on an industrial scale (Brandt et al. 2013). Some ILs were succeeded to be used as solvents, however, limited in large-scale application due to difficulty in solvent recovery and high cost (Francisco et al. 2012). Other than achieving low toxicity and biodegradability, ILs must be available at a lower cost (Sun et al. 2011), or to increase the efficiency in solvent recovery (da Costa Sousa et al. 2009). Brodeur et al. (2011) also concluded more studies are needed for decreasing the material cost of producing the ILs in a larger scale.

At the same time, Abbott et al. also introduced a novel green, deep eutectic solvent (DES) (Abbott et al. 2003) as an alternative to ionic liquids. DESs are the mixtures of compounds that have a significantly lower melting point than the starting materials due to the existence of a hydrogen bond (Dai et al. 2013). There are different kinds of HBDs which can be applied in the solvent synthesis, such as amides, acids, amines, and alcohols (Abbott et al. 2004). The combinations of cellular constituents in living organisms, such as sugars, amino acids and organic acids for the formation of DES are named Natural Deep Eutectic Solvents (NADES) (Choi et al. 2011). This established the theory that DESs can be synthesized using naturally existing components. Hence from an environmental aspect, these components are the ideal sources for DES. The design of DES is highly flexible as there is a wide range of components to be used for the synthesis of solvents (Durand et al. 2015). Other than the species of starting materials, an extra degree of freedom is given as the solvents’ structures can be customized by changing the ratio of the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) (Francisco et al. 2013).

In the year 2012, Francisco et al. proposed a new term, low transition temperature mixtures (LTTMs) (Francisco et al. 2012). The only distinction point from DES is LTTMs show glass transition temperature

instead of a melting point. LTTM also consists of at least one HBD and HBA that forms a mixture with a very low freezing point compared to the starting materials (Yiin et al. 2016). Francisco et al. (2012) also applied the LTTMs as solvents in the extraction of lignocellulosic biopolymers. The outcome of the study proved that certain LTTMs are capable of extracting a fair amount of lignin, but poor solubility to cellulose. Hence, the selectivity of separation of lignin to cellulose is very high.

The main objective of this project was to determine the compatibility of the natural plants malic acid such as papaya, cactus and luffa cylindrica with hydrogen bond acceptors such as L-proline, L-histidine, glycine and choline chloride for the synthesis of LTTMs. The capacity of LTTMs for solubilizing biopolymers was also tested. The hydrogen bonding and thermal stability of LTTMs with the highest lignin solubility capacity were analyzed and discussed. The preliminary delignification experiment was also conducted on the grinded empty fruit bunches from oil palm mill. This chapter opens up an opportunity for a simple, cheap and environmentally favorable biomass pretreatment method with a high degree of freedom.

METHODS

Raw Material and Chemicals

Empty fruit bunches (EFB) obtained from a palm tree plantation area in Perak, Malaysia were processed and ground to a particle size of 0.5 to 1 mm using FRITSCH cutting mill. Based on the structural content analysis of EFB from Forest Research Institute Malaysia (FRIM), it consisted of 26.9% hemicellulose, 26.6% cellulose, 25.4% lignin and 21.1% extractives and ash.

The natural plants extract such as papaya, cactus and luffa cylindrica (10 kg herb to the extraction of 1 kg powder) were supplied by Benua Sains Sdn Bhd as the source of HBDs. The HBAs, L-proline (> 98.5%), L-histidine (\geq 99%), glycine (> 99%) and choline chloride (\geq 98%) were obtained from Advance Altimas Sdn. Bhd. The lignin (alkali, low sulfonate

content), cellulose (90%) and starch (practical grade) used for the screening of biopolymers solubility capacity were purchased from Kemas Kurnia (M) Sdn. Bhd.

Synthesis of Natural LTTMs

HBA, HBD, and water were mixed together in a molar ratio of 1:1:10. The mixture was heated up in a water bath at 80°C while stirring continuously for 10 minutes. The preparation steps were repeated using different molar ratios of HBD to HBA as shown in Table 1.

Table 1. Combinations of HBD and HBA

Hydrogen Bond Donor	Hydrogen Bond Acceptor	Ratio of HBD to HBA
L-Malic Acid (Cactus)	L-Proline	1:1
	L-Histidine	2:1
	Glycine	3:1
	Choline Chloride	
L-Malic Acid (Papaya)	L-Proline	
	L-Histidine	
	Glycine	
	Choline Chloride	
L-Malic Acid (Luffa Cylindrica)	L-Proline	
	L-Histidine	
	Glycine	
	Choline Chloride	

Biopolymers Solubility Study

The solubility of biopolymers (lignin, starch, and starch) in LTTMs was determined by cloud point method. Vials containing 1.5 g of LTTMs were placed into an oil bath at 60°C. Around 0.2g of biopolymers was added continuously to the LTTMs. The solvent was stirred continuously throughout the biopolymers addition process to ensure good contact between the solutes and solvents. When undissolved biopolymers solutes first appeared in the mixture, the addition process was stopped. The mixture was kept stirring for 24 hours under the same temperature (60°C).

Solubility was confirmed if the undissolved solutes did not dissolve into the solvent after 24 hours. The experiment was repeated for all LTTMs at different molar ratios combinations using three different biopolymers.

Characterization of LTTMs

Fourier transform infrared spectroscopy (FTIR) analysis was conducted by spectrophotometer (Perkin Elmer Model Spectrum One/BX) in the range of 4000-500 cm^{-1} using a KBr disc containing 1% of finely ground samples to ensure the formation of hydrogen bonding in LTTMs. The thermal behavior of LTTM was determined using TGA-EXSTAR 6300 within the temperature range of 40 to 800°C, at a heating rate of 20°C min^{-1} with nitrogen as the carrier gas at a flow rate of 250 ml min^{-1} .

Pretreatment of Empty Fruit Bunches

A 300 mg grinded empty fruit bunches of size between 0.5 to 1 mm was added into 3 g of LTTMs and heated at 60°C in an oil bath for 24 hours while stirring continuously using magnetic stirrer. The mixture was cooled to room temperature and washed with ethanol for two to three cycles and then centrifuged in order to separate the supernatant layer and undissolved biomass. The LTTMs was recovered by removing the ethanol in the solvent mixture through rotary evaporation. The weight of lignin extracted in the supernatant layer was determined and the undissolved biomass was dried in an oven until it showed constant weight.

RESULTS AND DISCUSSION

Reproducibility of Natural Malic Acid for the synthesis of LTTMs

36 different LTTMs were synthesized using different types and combinations of HBD and HBA with their reproducibility shown in Table 2.

Table 2. Reproducibility of Natural Malic Acids

HBD	HBA	Ratio of HBD:HBA	Remark
Cactus	Proline	CP 1:1	Dissolved
		CP 2:1	Dissolved
		CP 3:1	Dissolved
	Glycine	CG 1:1	Dissolved
		CG 2:1	Dissolved
		CG 3:1	Dissolved
	Choline chloride	CC 1:1	Dissolved
		CC 2:1	Dissolved
		CC 3:1	Dissolved
	Histidine	CH 1:1	Crystallized
		CH 2:1	Crystallized
		CH 3:1	Crystallized
Luffa Cylindrica	Proline	LP 1:1	Dissolved
		LP 2:1	Dissolved
		LP 3:1	Dissolved
	Glycine	LG 1:1	Dissolved
		LG 2:1	Dissolved
		LG 3:1	Dissolved
	Choline chloride	LC 1:1	Dissolved
		LC 2:1	Dissolved
		LC 3:1	Dissolved
	Histidine	LH 1:1	Crystallized
		LH 2:1	Crystallized
		LH 3:1	Crystallized
Papaya	Proline	PP 1:1	Dissolved
		PP 2:1	Dissolved
		PP 3:1	Dissolved
	Glycine	PG 1:1	Dissolved
		PG 2:1	Dissolved
		PG 3:1	Dissolved
	Choline chloride	PC 1:1	Dissolved
		PC 2:1	Dissolved
		PC 3:1	Dissolved
	Histidine	PH 1:1	Crystallized
		PH 2:1	Crystallized
		PH 3:1	Crystallized

The starting materials were dissolved completely in water without the formation of residues. However, combinations of histidine formed crystals after the mixtures cooled down to room temperature. The crystallization might be due to the incompatibility of histidine to form a hydrogen bond with malic acid. As reported in Francisco et al. (2013), crystallization was prevented by hydrogen bonding formed between the starting materials. Hence, histidine is not suitable to be paired with natural malic acid in the synthesis of LTTMs.

Biopolymers Solubility Test

Biopolymers solubility test is a very important procedure to screen the capability of LTTMs to extract lignin from lignocellulosic biomass. LTTMs with the highest lignin solubility capacity were expected to have the best performance in extracting lignin from oil palm biomass. Solubility capacity of lignin, starch (hemicellulose) and cellulose in LTTMs were tested and the results are tabulated in Table 3. The results show that the solubility capacity was tuned according to the type of starting materials and different molar ratios used. Generally, all the LTTMs displayed a similar trend for the solubility of the biopolymers where lignin has the highest solubility capacity compared to starch and cellulose. Besides, cellulose was insoluble in all LTTMs as the particles still visible in the solvent even after stirring for 24 hours. The solubility of starch was negligible in all LTTMs, ranging from 0 to 2 wt%. As portrayed through the biopolymers solubility test, LTTMs have higher selectivity to lignin, hence it can be concluded that LTTMs is capable to extract mainly lignin from the biomass.

Effects of Sources of HBD on LTTMs

Figure 1 shows that the lignin solubility capacity of the HBDs studied in this work were comparable with each other where they showed highest lignin solubility when pairing with proline followed by choline chloride and then glycine. The LTTMs derived from cactus malic acid performed

better than the other two types of malic acid with the lignin solubility capacity of 12.87 wt% (CP 1:1). This result corresponds to the findings of Yiin et al. (2016b) where the malic acid extracted from cactus through microwave-assisted hydrothermal technique showed the highest lignin solubility capacity when it was used as the source of HBD for the synthesis of solvents. In addition, all the HBDs were incompatible with histidine as HBA due to the crystallization of mixtures after cooled down to room temperature. Hence, the lignin was not soluble in the remaining liquid portion of the solvent. This phenomenon was presumably due to no formation of hydrogen bonding between the starting materials. Francisco et al. (2012) also obtained similar results where the LTTMs derived from malic acid and histidine showed zero lignin solubility.

Table 3. Solubility values in wt% for lignin, starch, and cellulose for LTTMs

Sample	Biopolymers Solubility (wt%)			Sample	Biopolymers Solubility (wt%)		
	Lignin	Starch	Cellulose		Lignin	Starch	Cellulose
CP 1:1	12.87	0.33	0.00	LC 1:1	3.67	0.33	0.00
CP 2:1	9.33	0.47	0.00	LC 2:1	2.53	0.20	0.00
CP 3:1	6.13	0.80	0.00	LC 3:1	2.07	0.00	0.00
CG 1:1	3.67	1.87	0.00	LH 1:1	-	-	-
CG 2:1	3.20	0.67	0.00	LH 2:1	-	-	-
CG 3:1	2.07	0.53	0.00	LH 3:1	-	-	-
CC 1:1	7.60	0.33	0.00	PP 1:1	10.93	0.60	0.00
CC 2:1	6.00	0.20	0.00	PP 2:1	10.67	0.27	0.00
CC 3:1	4.73	0.00	0.00	PP 3:1	7.40	0.47	0.00
CH 1:1	-	-	-	PG 1:1	5.20	0.47	0.00
CH 2:1	-	-	-	PG 2:1	2.07	0.73	0.00
CH 3:1	-	-	-	PG 3:1	1.27	0.27	0.00
LP 1:1	11.53	1.20	0.00	PC 1:1	6.40	0.13	0.00
LP 2:1	10.00	1.87	0.00	PC 2:1	4.47	0.53	0.00
LP 3:1	6.00	2.13	0.00	PC 3:1	0.93	0.33	0.00
LG 1:1	5.13	0.53	0.00	PH 1:1	-	-	-
LG 2:1	5.40	0.40	0.00	PH 2:1	-	-	-
LG 3:1	1.33	0.20	0.00	PH 3:1	-	-	-

Effects of Molar Ratios of Starting Materials on LTTMs

Figure 1 shows that the solubility of lignin was decreased with an increased molar ratio of HBD. Lignin solubility capacity increased in the order of molar ratio 3:1 < 2:1 < 1:1. Out of 9 sets of different combinations of starting materials (CP, CC, CG, LP, LC, LG, PP, PC, PG), 8 sets of LTTMs showed that ratio 1 to 1 (HBD to HBA) had better performance than 3 to 1. This result was supported by the findings of Francisco et al. (2012) where the LTTMs with a higher ratio of HBA showed higher lignin solubility capacity. Generally, the solubility of starch in LTTMs was very low, while cellulose was insoluble in all the LTTMs. Based on the biopolymers solubility screening test, high efficiency of lignin extraction from biomass delignification was achievable using the LTTMs due to the negligible solubility of starch and cellulose.

Characterization of LTTMs

FTIR Analysis

The LTTMs (CP 1:1, PCC 3:1, LP 1:1) disclosed identical spectra for FTIR analysis (See Figure 2). The representative peak for the carboxylic acid group (-COOH) of malic acid was observed at around 1690 to 1760 cm^{-1} for the C=O group, which was responsible for the formation of hydrogen bonding. Besides, the broaden peak at around 2700 to 3800 cm^{-1} contributed by the stretching vibration of hydroxyl (-OH) group was also due to the interaction of hydrogen bonding (Francisco et al. 2012).

Kubo and Kadla (2005) mentioned that the hydrogen bonding is important to the variation in properties of biopolymers. The bonding structure varies with the types of lignocellulosic biomass such as softwood or hardwood. Thus, the hydrogen bonding in the solvents was able to alter the bonding structure in lignin and further extracted it from biomass. More studies are needed to be carried out in order to have a deep understanding of the molecular structure of both the solvents and lignin.

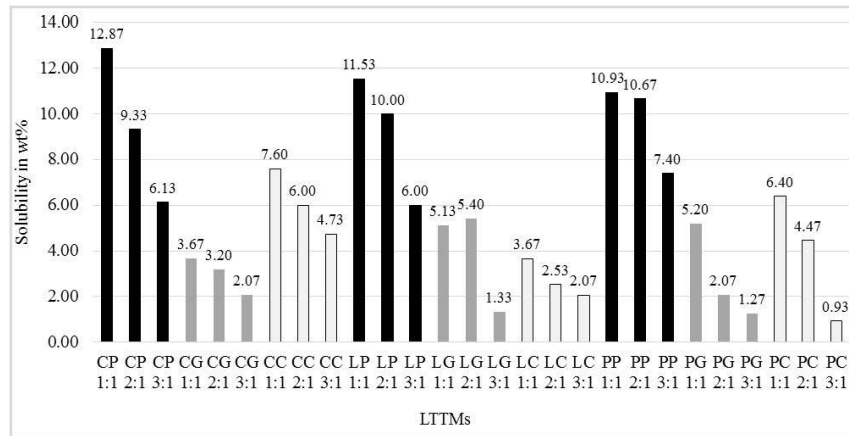


Figure 1. Lignin Solubility Capacity of LTTMs.

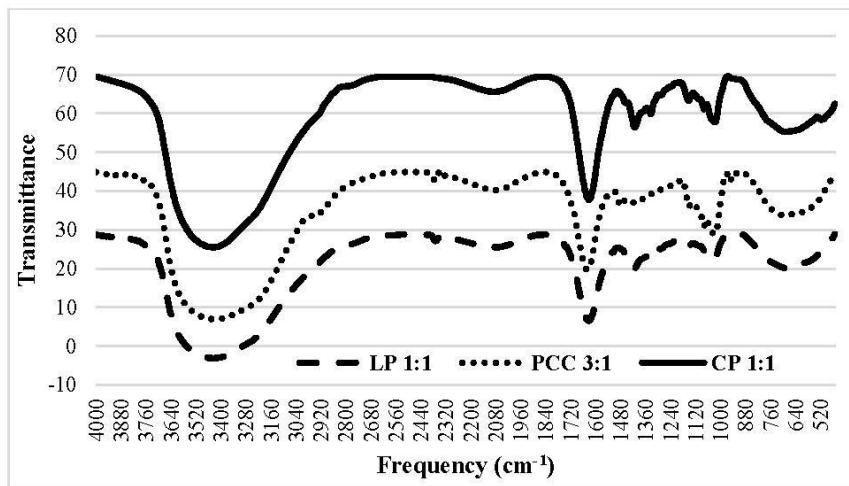


Figure 2. FTIR spectra of LTTMs.

Thermogravimetric Analysis (TGA)

The most significant disadvantage of LTTMs was the thermal instability of solvent (Francisco et al. 2013). Figure 3 shows that CP 1:1 and LP 1:1 started to decrease in weight drastically at around 60°C. CP 1:1 and LP 1:1 were categorized as thermal instable solvents due to the weight loss at increasing temperature. Asymmetrically, PCC 3:1 has lower

degradation rate at the first inflection point than CP 1:1 and LP 1:1. Nonetheless, it also showed a higher rate of degradation at a second inflection point which might be due to the higher molar ratio of HBD (Yiin et al. 2016a). The LTTMs with the structures formed by hydrogen bonding were expected to show lower thermal stability. The strength of chemical bonds was decreasing with increasing temperature. The biggest change of weight in LTTMs occurred at first inflection was due to the vaporization of water. The second inflection point was due to the degradation of acid groups (Mano et al. 2015) or functional groups with oxygen content (Hayyan et al. 2015) at high temperature. Comparing the result trend graph between the result and user manual from Mason Technology, the result belongs to a type of moisture escape on melting. However, the reaction contributing to significant weight loss is not exactly conclusive. This phenomenon might be due to either chemical reaction or physical transition which is a crucial subject to be studied in the future.

Biomass Delignification

Figure 4 shows the LTTMs turned into darker color after the pretreatment process. Upon adding ethanol and centrifuged, the extracted lignin was separated out from the delignified biomass and solvent. The LTTMs was then recovered by removing the ethanol from solvent using rotary evaporator while undissolved biomass put into an oven.

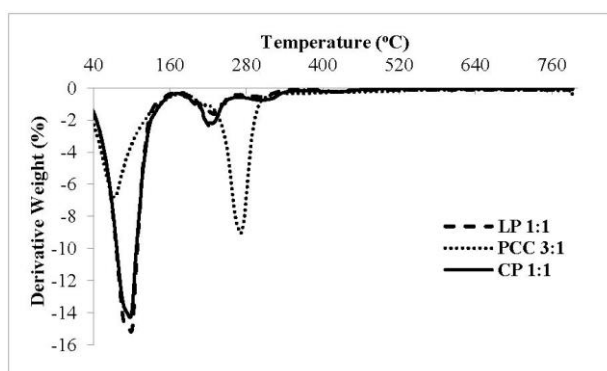


Figure 3. DTG curves of LTTMs.



Figure 4. Biomass processing with CP 1:1 at different stages (From left: Before stirring, after overnight treatment, after centrifuging with ethanol).

An 86.67 wt% of non-dissolved biomass was recovered after the dried completely in the oven. CP 1:1 was able to extract 13.3 wt% of lignin from oil palm empty fruit bunch. The result is comparable to the biopolymers solubility test where CP 1:1 was able to dissolve 12.87 wt% of lignin. The solubility difference between oil palm biomass and chemically graded lignin might be due to the difference in chemical structures and bondings.

CONCLUSION

A new generation of green solvents, LTTMs, were synthesized naturally and with biodegradable materials. The malic acids from plant extracts such as cactus, papaya, and luffa cylindrica were compatible with proline, choline chloride and glycine for the synthesis of LTTMs. Cactus malic acid showed better performance as a source of HBD, especially when paired with proline as an HBA with the lignin solubility of 12.87 wt% and negligible starch and cellulose solubility. The FTIR spectra showed that -COOH and -OH groups are the dominant bonding structure. These two functional groups were attributed to the formation of hydrogen bonding. Besides, the DTG curves verified the maximum allocation of temperature for biomass delignification. The most ideal combination of LTTMs (CP 1:1) was able to extract 13.3 wt% of lignin from oil palm

biomass. Hence, LTTMs have the outweighed advantages in the nature of solvent properties and economic and environmental consideration.

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