Prediction of solvation properties of low transition temperature mixtures (LTTMs) using COSMO-RS and NMR approach

N R Yusuf¹, S Yusup¹,², C L Yiin³, P J Ratri⁴, A A Halim¹ and N A Razak¹

¹ HIcoE-Centre for Biofuel and Biochemical Research (CBBR), Institute of Self-Sustainable Building,Universiti Teknologi PETRONAS (UTP), 32610, Bandar Seri Iskandar, Perak, Malaysia
² Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), 32610, Bandar Seri Iskandar, Perak, Malaysia
³ Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering,Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan 94300, Sarawak, Malaysia
⁴ Chemistry Department,Universitas Pertamina, Jl Teuku Nyak Arief, Simprug, Jakarta Selatan, 12220, Indonesia

Email: drsuzana_yusuf@utp.edu.my

Abstract. The concept of sustainable and green solvent has always highlighted in the field of energy and environmental science. The synthesis and application of natural-based Low Transition Temperature Mixture (LTTM) as a novel and green solvent for the lignocellulose biomass pre-treatment such as delignification of Oil-Palm Empty Fruit Bunch (EFB) have been greatly emphasized. In this present work, the investigation of LTTM efficiency as green solvent in delignification process was conducted using both theoretical and experimental studies. Initially, screening of solvation properties of different types of hydrogen bond acceptor (HBA) and predicted hydrogen bond donor (HBD) for synthesis of LTTMs was conducted using conductor-like screening model (COSMO-RS) software and formation of hydrogen bonding was evidenced using NMR spectroscopy analysis. Three types of HBA namely sucrose, choline chloride and monosodium glutamate were mixed with malic acids as HBD and their charge density distribution on the surface was determined through sigma profile (σ). The COSMO-RS results determined the σ profile of pure component malic acid to be 11.42, sucrose to be 25.37 and the total value of σ profile for mixtures is 14.19 as the best combination of LTTM composition compared to LTTM from choline chloride and monosodium glutamate (MSG). The reliability of the COSMO-RS predictions data was correlated with Nuclear Magnetic Resonance (NMR) analysis through determination of peaks with chemical shifts hydrogen bonding that suggested existence of potential interaction between malic acids and sucrose has occurred.

1. Introduction

The dependency of fossil fuels leads to the environment problems such as environmental contamination and global heating. Thus, most researchers are looking for bio-based materials that can offer renewable, biodegradable, and biocompatible sources as alternative to fossil based materials. According to researchers Ong & Wu [1] Zhang et al. [2], Zakzeski et al. [3] and others, lignocellulosic biomass as
feedstock for bio-chemicals and fuels conversion as the alternative to fossil feedstocks increasing yearly. Malaysia is one of the countries that can capitalize the renewable energy resources based on resources availability of the biomass generated from the plantations and the mills. Malaysia generated at least 168 million tons yearly from their biomass, including timber and oil palm waste, rice husk, coconut trunk fibers, municipal waste and sugarcane bagasse [4–6]. Among all this lignocellulosic biomass, oil palm has the biggest contribution towards Malaysia’s economy. Only 10% of the total palm oil can be recovered. Another 90% biomass such as oil palm trunk (OPT), oil palm fronds (OPF), mesocarp fiber (MF), palm oil mill effluent (POME) and empty fruit bunch (EFB) is considered as wastes. Among this palm oil biomass, based on researchers data [7,8], empty fruit bunch (EFB) is one of the most abundant lignocellulosic biomass.

Lignocellulosic biomass attracted wood industry as an alternative fiber as it is most abundant feedstock worldwide and they contain of 35-50% cellulose, 35% hemicelluloses, 5-30% lignin [9,10]. Researchers also showed growing interest in lignocellulosic biomass conversion which contributed to successful production in renewable chemicals and biorefining technologies. Hence, an efficient conversion technology is crucial to produce high conversion bio-chemicals. The technologies involved chemical or enzymatic treatments which required high temperature and pressure are judged as low efficiency and expensive. Delignification process is one of conversion method that hydrolyzed the hardwood. Delignification efficiency depends on variables namely reaction temperature and time. The bonding of lignin usually broken down under lower temperature. Higher temperature should be avoided as it will reduce cellulose purity through the byproduct formation. There are few solvent used in the delignification process such as ionic liquid, deep eutectic solvent (DES) and Natural deep eutectic solvents (NADES) [11,12]. Natural deep eutectic solvent (NADES) is bio-derived deep eutectic solvent which comprised of two or more compounds such as organic acid, sugar, alcohols, amines, and amino acid. The deep eutectic identified as a mixture of solid compound transformed to liquids that have lower melting point than room temperature. These unique properties resulted NADES as alternative solvent in many applications as conventional solvents is generally avoided because of toxicity issue [13]. On the other hand, a new approach was introduced which is low-transition-temperature-mixtures (LTTMs) solvent. LTTMs helps to break lignocellulosic structure and lead to the dissolution effectively. Compared to NADES, LTTMs showed higher biocompatibility, low toxicity, lower cost, and it requires less time to prepare. Other than that, the delignification process is viable with LTTMs as its existing hydrogen-bond can disrupt the lignocellulose chain of lignin which contributed by formation hydrogen bond between LTTMs and biomass [14,15].

To access the solvation properties and potential of hydrogen bond of LTTMs, the effect of LTTMs components in prediction potential hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) was evaluated using solvation-thermodynamics molecular simulation. COSMO-RS is one of solvation simulation model which can be used as screening model of molecular interaction among pure components and components in mixtures [16–18]. Thus, in this present work, COSMO-RS simulation was employed to compute the value of the σ profile of monosodium glutamate, sucrose, and choline chloride with malic acids. Reliability of COSMO-RS predictions data was correlated with Nuclear Magnetic Resonance (NMR) analysis to determine the formation of hydrogen bonding in LTTM as well as to prove rationalization of solvation behavior. In this sense, screening of the most ideal HBD and HBA, for synthesis of LTTMs through COSMO-RS simulation and correlation with NMR analysis are important to discover the efficiency of natural LTTMs for biomass delignification.

2. Methodology

2.1. COSMO-RS computation model

COSMO-RS computational (Amsterdam Modeling Suite 2019.3) was calculated the chemical potentials of the molecules within liquid solutions or to predict the solvation properties of pure compound and mixed fluids. The COSMO-RS data estimates other important thermodynamic parameters, such as solubility or activity coefficient. In this study, sets of LTTMs (malic acid:sucrose:water, choline
chloride:sucrose:water and monosodium glutamate:sucrose:water) were used for validation of the model. Compositions and weight ratio of the LTTMs used in the study are shown in table 1.

Table 1. Ratio of the LTTMs component used in the study [19].

| HBA        | HBD        | A Solvent | Weight Ratio |
|------------|------------|-----------|--------------|
| Sucrose    | Malic Acid | Water     | 2:1:1        |
| Choline Chloride | Malic Acid | Water     | 2:1:1        |
| Monosodium Glutamate | Malic Acid | Water     | 2:1:1        |

2.2. Theory and Background
The molecular interaction between pure compound of HBA, HBD and their solvent in table 1 is based on interaction surface segments of the molecules. This interaction surface segment is determined by the surface charge density distribution of the molecules which calculated from Quantum mechanical calculation in the COSMO-RS simulation [20,21]. The created surface segments from the each molecules is indicated by their screening density charge and area. The main parameters in calculating the total interaction energy between the compounds are hydrogen bonding, the electrostatic misfit, and van der Waals interactions. Sigma profile (σ-profile) is surface composition function unit for calculation of screening charge density distribution on the surface [20]. The whole σ-profile system namely $P_s(\sigma)$ can be then described as the sum of the σ-profiles of its individual components weighted by their molar fractions. These calculated by chemical potential of the surface ($\mu_s$) and expressed as equations below.

$$\mu_s = -\frac{RT}{a_{\text{eff}}} \ln \left[ P_\sigma(\sigma') \exp \left( \frac{a_{\text{eff}}}{RT} \left( \mu_s(\sigma') - e(\sigma, \sigma') \right) \right) d\sigma' \right]$$  \hspace{1cm} (1)

Where,

$$e(\sigma, \sigma') = E_{vdW}(\sigma, \sigma') + E_{HB}(\sigma, \sigma') + \frac{E_{MF}(\sigma, \sigma')}{a_{\text{eff}}}$$  \hspace{1cm} (2)

Where, $E$ for Elastic modulus, intramolecular forces and also dispersive, van der Waals (vdW), $d$ is diameter of material, $a_{\text{eff}}$ for effective segment radius, $E_{MF}$ for misfit energy, $E_{HB}$ for hydrogen bonds energy, $T$ for temperature.

2.3. Computational Details
In this work, molecular structure of the pure compounds that include malic acids and sucrose was obtained from the chemical structure in Amsterdam Data Function (ADF) database. However, chemical structure of choline chloride and monosodium glutamate are not available in the ADF library thus musvt be generated using ADF input program. Fast σ profile can be determined for the component that existed in the library by using the chemical abstract service (CAS) and simplified molecular-input line entry (SMILE). These information and structure of the compounds were summarized in table 2.

COSMO-RS estimation were set by Amsterdam Data Function (ADF)-COSMO result files and generated by following computational program. The ADF-Graphical User Interface (ADF-GUI) function was applied for the quantum-chemical calculation to initiate the COSMO files for choline chloride and monosodium glutamate compound. Density functional theory (DFT) is important to optimize the compound molecular geometry at the DF module. Therefore, this optimization applied Beck-Perdew (GGA:BP86) density functional theory and related to triplezeta polarized (TZP). Klamt radii, and Delysurface area for atoms were used in the calculations until the compound converged [16,17,22]. Subsequently, the obtained geometries of these compounds were further analysed. The
molecular surface polarity distributions (σ-profiles), and other thermodynamical properties behaviour can be calculated and obtained at given temperature with reference to the retrieved from COSMO output files.

2.4. LTTM Experimental Methodology
LTTM preparation followed the optimum condition and procedure by Yiin et al. [19]. Malic acid, sucrose and water were mixed in a ratio of 1:2:1, respectively in a beaker and stirred. The temperature was set to 60°C while stirring speed was set to 300 rpm and the process continues until mixture become a clear liquid at around 30 minutes. Another two combination of HBDs and HBAs were used in preparation of LTTMs solvent followed same optimum condition. The HBD and HBA compounds used were summarized in table 2.

Table 2. Compositions and molar ratio of the LTTMs used in the study.

| Component | CAS    | SMILE | Structure |
|-----------|--------|-------|-----------|
| Malic Acid | 6915-15-7 | C(C(=O)O)O)(=O)O | ![Malic Acid Structure](image) |
| Sucrose   | 57-50-1  | C(C1C(C(C(O1)OC2(C(C(C(O2)CO)O)O)CO)O)O)O | ![Sucrose Structure](image) |
| Substance                        | CAS No. | Chemical Structure                                      |
|---------------------------------|---------|---------------------------------------------------------|
| Choline Chloride                | 67-48-1 | ![Chemical Structure of Choline Chloride](image)          |
| Monosodium Glutamate            | 142-47-2| ![Chemical Structure of Monosodium Glutamate](image)     |

**2.5. NMR Spectroscopy**

H NMR spectroscopy analysis was performed using a Bruker DRX-500 spectrometer (500 MHz) and TMS as a calibration standard at room temperature. All spectra were recorded using Nuclear Magnetic Resonance Bruker AVANCE 400 MHz III operating at 400.17 MHz. Approximately of the sample is dissolved in 0.6 mL of Toluene-d8 and the dissolved solution was put into a NMR tube with 5-mm diameter. 1H NMR spectra were taken using 7.5-degree pulse angle, 2.5 s recovery delay, and 32 scan times. Measurement conditions were 90-degree pulse angle and 200 scan times.

**3. Result and Discussion**

In this work, the pure compound and mixture of LTTM was validated through COSMO-RS simulation and NMR analysis. The screening of pure compound and the mixture of LTTMs were performed via thermodynamic properties (i.e., infinite dilution and activity coefficients) to identify the most suitable interaction for solvating. Based on the theory and computational details, the compounds were obtained using Turbomole BP/TZVP. The COSMO-RS charge density was calculated by averaging the results for all cases. Calculation for the charge distribution showed that using different models resulted in different mixture behaviour restive of the activity coefficient at infinite dilution and sigma profiles.
3.1. COSMO-RS Simulation

3.1.1. Activity Coefficients of Pure Compounds. The selection of solutes for synthesis LTTM was based on Activity coefficients unit at infinite dilution. They reflected the interaction between LTTMs materials because the solute–solute interaction can be negligible at infinite dilution. Thus, in this work, activity coefficients of solutes in LTTMs at infinite dilution collected from experimental data from previous study by Yiin [14] is referred to optimize the COSMO-RS model parameters. Thus, regression of the interaction parameters of the component was done. Their precision were based on interaction of computed thermodynamic quantities with measured solubility data. Three different types of mixtures were suggested in this work which involved pure compound of malic acid, choline chloride, monosodium glutamate and sucrose. Table 3 showed the activity coefficient of these compound and the values are close to ideal behaviours in liquid phase [16]. Furthermore, the mixture’s behaviours and performance of all compounds of each model was validated against the experimental data through sigma profile and hydrogen bonding of the components.

Table 3. The activity coefficient of LTTM compound from COSMO-RS.

| Component                  | Activity Coefficient, Γ |
|----------------------------|-------------------------|
| Malic Acid                 | 1.340                   |
| Sucrose                    | 6.945                   |
| Choline Chloride           | 10.692                  |
| Monosodium Glutamate       | 25.210                  |

3.1.2. Sigma Profile and Hydrogen Bonding of Pure Compounds Coefficients of Pure Compounds. Sigma profile described the charge density distribution (σ-profile) which is a mathematical calculation of molecule’s polarity. Thin peaks in the σ-profiles illustrated to low polarity, whereas wide peaks indicate high polarity [16,17,22] as displayed in figure 1. figures 2 (a), (b) and (c) showed σ-profiles of the HBAs and HBDs used in this work. The σ-profile can be segregated into three main regions: (i) the HBD region, positive charge densities (blue surface colour) in the range of -∞ < σ < -0.0082 [eA·2] correspond to the hydrogen donating surface. (ii) the nonpolar region described almost neutral charge densities and (iii) the HBA region, negative charge densities (red in colour), in the range of -0.0082 < σ < 0.0082 [eA·2]: correspond to polar regions. Figure 2, 3 and 4 showed the sigma profile of choline chloride, monosodium glutamate and sucrose. Generally, based on the figures shown, all of compound indicated in the HBA region and sucrose showed highest value of sigma profile of 25.373, followed by choline chloride at 20.134 and monosodium glutamate of 12.223. The hydrogen bonding parts of the components are also illustrated in figure 2, 3 and 4. The hydrogen peaks of choline chloride, sucrose and monosodium glutamate also fall in the hydrogen bond acceptor (HBA) region which shows the highest peak is on the right side of the graph. The hydrogen bond part sigma profile for all compounds also determined that sucrose showed the highest value of 11.095 compared to monosodium glutamate of 10.124 and choline chloride of 1.665. Thus, this result indicated sucrose has the higher tendency to accept more hydrogen compared to others. The screening was repeated for the mixtures.
Figure 1. Chemical information processed by the COSMO-RS method [23].
Figure 2. (a) Sigma profile for choline chloride pure component and (b) Sigma profile for monosodium glutamate pure component and (c) Sigma profile for sucrose pure component.

Figure 3 (a), (b) and (c) showed the sigma profile for the HBA of sucrose, monosodium glutamate and choline chloride with malic acids. Generally, all mixtures showed high sigma profile values which indicated high attraction to H-bond acceptor group and H-bond donor in mixtures. Figure 3 (a) showed positive values of the σ-profiles between the regions σ 0.002 and σ 0.02 e/Å², indicating the presence of the oxygen atoms within the molecules that responsible for accepting the hydrogen atoms and forming the hydrogen bond of choline chloride. The H-bond donor character which appears from the hydroxyl group of the malic acids was presented by a low intensity peak at −0.01 and −0.019 on their sigma profile. The results correspond with another researcher’s finding [24]. Figure 3 (b) showed σ-profiles of monosodium glutamate at region 0.005 and 0.02 e/Å² and HBD σ-profiles of malic acids as described at -0.01 and -0.022. Figure 3 (c) determined high intensity sigma profile for HBA.
This described the high interactions between malic acids and sucrose through formation of hydrogen bonds as compared to others HBA (choline chloride and monosodium glutamate) [16,19,25].

The solvation and interaction between solute and solvent study are a complex process, as they be influenced by several factors. In the view of thermodynamic terms, increasing dissolution tendency illustrated in previous COSMO-RS sigma profile showed stronger hydrogen bonding among the HBA and HDA constituents. Furthermore, NMR spectroscopy was applied to verify hydrogen bonding which involved in this interaction [26,27]. Thus, determination of hydrogen bond detection of H bond donor and acceptor were carried out and utilized the same frequencies as for hydroxyl proton detection. Table 4 and figure 4 showed chemical shift component and H-NMR spectroscopy of sucrose compound. Table 5 and figure 5 showed chemical shift component and H-NMR spectroscopy of malic acids compound. The up field in the signals of characteristic hydroxyl protons in sucrose and malic acids reflect the
hydrogen bond structures existence. The downshift and intensity of characteristic group were indicative of many hydrogen bonding emerged between HBA and HBD [27]. This indicated that there were large hydrogen bond structures comes from (OH$^-$ ions in sucrose as HBA and the hydrogen malate of acids malic as the HBD. The high intensity of peak in the sucrose spectra indicated that a part of the protons of D$_2$O.

Similar observation has been explained by Christofides et al. [28], whereby peaks of methyl and methylene groups was observed in downfield shift spectra, and the relative number of protons detection on the hydroxyl groups which relative to the protons on the methyl group. Therefore, it is indicated the hydrogen bonding donor in malic acids, and oxygen atom from hydroxyl groups for accepts a hydrogen bond. Both group are important to made stronger bonding as compare to the compound that consist oxygen atom as donor group only. These observations provide suggestion of interaction of the COOH bonds of malic acids will form a hydrogen bond with hydroxyl group of sucrose compound. The result are in agreement with review paper by Espino et al. [11]. They concluded that although LTTM NADES can be derived from prepared from different routes, the same chemical shift will be showed in $^1$H NMR spectra but with same HBA/ HBD components.

**Table 4.** Summary of H-NMR with possible sucrose component.

| Chemical shift | Splitting | Integral | No of H | (refer to H-NMR chemical shift diagram) |
|----------------|-----------|----------|---------|---------------------------------------|
| 5.2-5.3        | 2         | 1.00     | 1       | (-OH), (C=C-H)                        |
| 4.0-4.1        | 2         | 1.02     | 1       | (-OH), (-CH2-O)                      |
| 3.9            | 3         | 1.03     | 1       | (-OH), (-CH2-O)                      |
| 3.7-3.8        | 5         | 1.05     | 1       | (-OH), (-CH2-O)                      |
| 3.6-3.7        | 3         | 4.30     | 4       | (-OH), (-CH2-O)                      |
| 3.6            | 3         | 1.10     | 1       | (-OH), (-CH2-O)                      |
| 3.5            | 1         | 1.97     | 1       | (-OH), (-CH2-O)                      |
| 3.4            | 4         | 1.00     | 1       | (-OH), (-CH2-O)                      |
| 3.3            | 3         | 0.99     | 0       | (-OH), (-CH2-O)                      |
Figure 4. H-NMR spectrum for sucrose structure.

Figure 5. H-NMR spectrum for malic acids structure.
Table 5. Summary of H-NMR with possible malic acids component.

| Chemical shift | Splitting | Integral | No of H | Proposed Structures |
|----------------|-----------|----------|---------|---------------------|
| 4.3-4.4        | 3         | 1.00     | 1       | -OH                 |
| 2.5            | 8         | 2.14     | 2       | 2(-OH)              |

2(H-C=C=O)

4. Conclusion
In this study, COSMO-RS simulation was explored to forecast the solvation properties of LTTM compounds. It is possible to screen for most effective LTTMs based on the solvation power and $^1$H nuclear magnetic resonance (H-NMR) analysis. The H-NMR validated the hydrogen bonding presence. Generally, COSMO-RS software determined sigma profile of choline chloride, monosodium glutamate and sucrose in the hydrogen bond acceptor (HBA) region and sucrose showed highest value of sigma profile of 25.373, followed by choline chloride at 20.134 and monosodium glutamate of 12.223. The same results were indicated by the mixture compound of HBA in the presence of malic acids (HBD). High intensity sigma profile for HBA (Sucrose) at σ-profiles region of 0.007 and 0.0019 e/Å² and HBD (Malic acids) at region -0.001 and -0.021 e/Å² indicated great repulsion to both H-bond donor and H-bond acceptor group in the mixture. $^1$H nuclear magnetic resonance spectroscopy demonstrated that there was intensive hydrogen-bonding interactions between sucrose and malic acids based on signals reflected by the hydroxyl protons. The ‘up field’ region showed the hydroxyl protons signals in sucrose and malic acids in the hydrogen bond structure. The down field showed representative group were resulted of many hydrogen bonding formed between the components.

Acknowledgments
The authors gratefully acknowledge support from Ministry of Education Malaysia through HICoE award to CBBR centre, financial support for International Collaborative Research Funding (ICRF) grant and Universiti Teknologi PETRONAS for a URIF grant. The authors would also like to thank the laboratory technical assistants, and other staff, at the Biomass Processing Laboratory for their assistance.

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