Separation and purification of valuable chemicals from simulated hydrothermal conversion product solution

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

5-HMF as a versatile organic compound is considered as a promising biomass-derived value-added product via dehydration of saccharide. A large amount of research has been carried out on its production and separation. In this research, three single and three mixed solvents were tested to separate 5-HMF via liquid-liquid extraction from simulated HTC products. The mixed solvents were made up of DCM-THF, DCM-2-butanol and 2-butanol-THF with different mixing ratio of 1:4, 1:1, and 4:1. 20wt% and 10wt% NaCl were added in to help phase separation and to improve the performance of extraction. The simulated HTC product was composed of 5-HMF, levulinic acid and furfural. The extraction was carried out in vial and the phase separation was accomplished in a separatory funnel.

The aqueous phase was analyzed with HPLC-UV to determine the solute concentrations in the aqueous phase. The solute concentrations in organic phase, partition coefficients, separation factors, solute recovery rates and purities of 5-HMF in separated products were calculated accordingly. The separation performance of mixed solvents was compared with theoretical values. In addition, the effects of pH and NaCl concentration on extraction and separation were investigated.

It was found that the partition coefficients of 5-HMF were always higher than those of levulinic acid. 20 wt% of NaCl improved 5-HMF extraction significantly, and the corresponding partition coefficient was 6.87. Extraction of levulinic acid was found more sensitive to solvent pH value than 5-HMF and furfural. For 5-HMF extraction, pH 2.4 was more favorable than pH 2.0. Meanwhile, mixed solvents had better extraction performance than each single solvent for 5-HMF. The performance of the mixed solvents depended on mixing ratio; partition coefficient showed linear correlation with mixing fraction.

More furfural was extracted into organic phase than 5-HMF, and the partition coefficients of levulinic acid were very close to that of 5-HMF. In general, however, mixed solvent extraction was able to improve the extraction efficiency rather than separation efficiency of 5-HMF.

Acknowledgements

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To those I have worked together during my Master's research program, Jordan Scott, Ralph Dickhout and Victor Chabot, I would like to thank you for all the help and support, which gave me the enjoyable study and working environment.

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C_0 – initial concentrations of solute in simulated HTC product solution;

C_{aq} – solute concentration in aqueous phase after extraction;

C_{org} – solute concentration in organic phase after extraction;

C_{orgA} , C_{orgB} – solute concentration in solvent A and B of mixed solvent;

$[A^-]$ – concentration of dissociated ions of $A-$;

$[HA]$ – concentration of molecule form of HA;

$[HA]_0$ – initial total molecule concentration of HA;

HA – a general weak acid;

K_w – ionization constant of water;

M_A, M_B – mass of the solutes dissolved in solvents A and B, respectively;

M_{org} – total mass of solute in organic phase;

M_{total} – total mass of solute;

p – purity of 5-HMF;

P'_A, P'_B – polarity indices of solvent A and B, respectively;

P'_t – polarity index of mixed solvent;

P_A, P_B – partition coefficients of solute in solvents A and B, respectively;

P_0 – theoretical partition coefficient of mixed solvent;

pKa – acid dissociation constant;

P_{HMF} – partition coefficient of 5-HMF;

P_{LVA} – partition coefficient of levulinic acid;

P_{FF} – partition coefficient of furfural;

R – recovery rate;

S_1 – separation factor between 5-HMF and LVA;

S_2 – separation factor between 5-HMF and furfural;

Stdev – standard deviation;

V_0 – initial volume of simulated THC product solution;

V_{aq} – volume of aqueous phase;

V_{org} – volume of organic phase;

V_A, V_B – volume of solvent A and B;

x_A, x_B – volume fraction of solvent A and B in mixed solvent, respectively;

$f(x_A)$, $g(x_B)$ – function of volume fraction of solvent A (x_A) and B (x_B) , respectively;

$u(x_A)$, $v(x_A)$ – non-constant terms in $f(x_A)$ and $h(x_A)$, respectively;

m, n – constant terms in $f(x_A)$ and $h(x_A)$, respectively.

List of Abbreviations

5-HMF	5-(hydroxymethyl) furfural
[ASBI][Tf]	3-allyl-1-(4-sulfobutyl)imidazolium Trifluoromethanesulfonate
[BMIM][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM] Cl	1-butyl-3-methylimidazolium chloride
ChoCl	Choline chloride
CPO	Chloroperoxidase
DALA	5-aminolevulinic acid
DCM	Dichloromethane
DHMF	2,5-di(hydroxymethyl)furan
DHM-THF	2,5-di(hydroxymethyl) tetrahydrofuran
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
[EMIM] Cl	1-ethyl-3-methylimidazolium chloride
FA	Formic acid
FDA	2,5-furan dicarboxylic acid
FDC	Furan -2,5- dicarboxaldehyde
FF	Furfural
FFCA	5-formylfuran-2-carboxylic acid
HCl	Hydrochloric acid
HFCA	5-hydroxymethylfuran-2-carboxylic acid
[HMIM][Cl]	1-hexyl-3-methylimidazolium chloride
HMTHFA	5-(hydroxymethyl) tetrahydrofuran-2-carbaldehyde
HPA	Heteropolyacid
HPLC	High performance liquid chromatography
H_3PO_4	Phosphoric acid
H_2SO_4	Sulfuric acid
HTC	Hydrothermal conversion
LVA	Levulinic acid
LVE	Levulinic ester
MF	2-hydroxypropane-1,2,3-tricarboxylate (mumefural)

MIBK	Methyl isobutyl ketone
[NMM][CH_3SO_3]	N-methylmorpholinium methyl sulfonate
NREL	National Renewable Energy Laboratory
PBS	Buffer solution
PBT	Polybutylene terephthalate
PDA	Photodiode array
PET	Polyethylene terephthalate
TsOH	p-toluene sulfonic acid
THF	Tetrahydrofuran
VOP	$VOPO_4$•$2H_2O$
ZrP	Zirconium phosphate

Chapter 1

Introduction

1.1 Motivation

Biomass has been considered as a sustainable resource for energy supply, which provides 37TWh biomass renewable energy per year [1]. Biomass is also a renewable resource for the production of many valuable chemicals. In one report from United States, 30 chemicals produced from biomass were listed, and 12 of them were evaluated as the most valuable building blocks in chemical industry, including those from both fermentation and chemical conversion such as 5- (hydroxymethyl) furfural, levulinic acid, 2,5-furandicarboxylic acid and itaconic acid [2].

5-(Hydroxymethyl) furfural (5-HMF) has been chosen as the focus of this research due to its versatile applications in chemical industry. 5-HMF can be produced from glucose, fructose, cellulose and lignocellulosic biomass. It is an intermediate for many other products, including pharmaceutical products [3, 4], fungicides, flavor-enhancers in the food industry [5, 6], polymers [7-9], and alkane biofuels [10, 11]. Some of the reaction pathways are shown in Figure 1-1[12].

5-HMF and many of its derivatives possess a considerable market potential. The market price of 5-HMF is about \$700-\$1500 per kilogram. 2,5-Furan dicarboxylic acid (FDC) is regarded as a replacement of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) with a considerable market size [13]. As one of the co-products, levulinic acid has a worldwide market of about one million pounds per year with a price around \$10 per kilogram, while the cost of levulinic acid production can be reduced to \$3.21 per kilogram [14].

Despite the impressive array of useful 5-HMF-derived intermediate chemicals in literature, 5-HMF is still not produced at an industrial scale [15]. Although a great amount of research has been carried out for 5-HMF production, challenges exist not only in its production but also in separation.

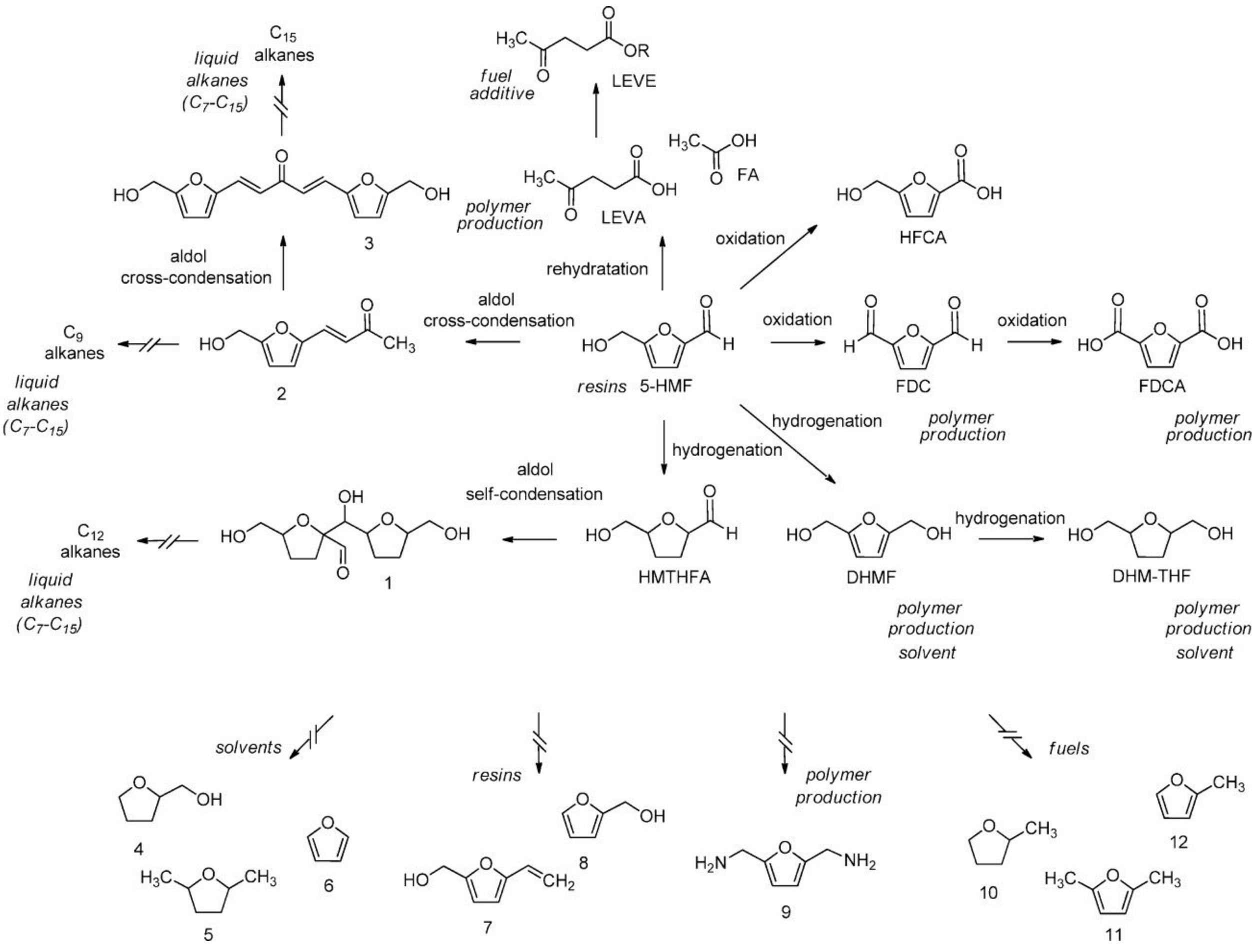

Figure 1-1. Chemistry and applications of 5-HMF and its derivatives

(solid arrow, direct transformation; broken arrow, multistep reaction; 5-HMF; LVA; LVE; FA; HFCA; FDC; FDCA; DHMF; DHM-THF; HMTHFA; 1,2-(hydroxy(5-(hydroxymethyl)tetrahydrofuran-2-yl)methyl)-5-(hydroxymethyl) tetrahydrofuran-2-carbaldehyde; 2, (E)-4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one; 3,(1E,4E)-1,5-bis(5-(hydroxymethyl)furan-2-yl)penta-1,4-dien-3-one; 4, tetrahydrofur-furyl alcohol; 5, 2,5-dimethyltetrahydrofuran; 6, furan; 7, 2-hydroxymethyl-5-vinylfuran; 8, furfuryl alcohol; 9, 2,5-di(aminomethyl)furan; 10, 2-methyl tetrahydrofuran; 11, 2,5-dimethylfuran; 12, 2-methylfuran)

1.2 Research opportunities and Contributions

A great amount of studies on 5-HMF production have been carried out, and some of them were summarized recently by Rosatella et al. [16]. 5-HMF can be produced with compressed hot water [17], organic solvents [18, 19] and ionic liquids [20-24] as reaction media. Compared with the application of organic solvents and ionic liquids, producing 5-HMF in a water solution, which is referred to as hydrothermal conversion (HTC), is considered as a “green” process. However, it is difficult to maintain both a high conversion of feedstock and a high selectivity of 5-HMF production in HTC under the same condition.

Most previous and on-going research focuses on improving the production efficiency of 5-HMF [21, 25-28], but separation and purification of 5-HMF still remain a challenge. Several technologies have been developed to address this challenge, including synthesis in ionic liquids [20, 21] or supercritical fluids [29], separation with preparative chromatography [30], or absorption by sorbents [31].

In this work, mixed organic solvent extraction was applied to the extraction of 5-HMF from its simulated product solution. The extraction performance was improved by using mixed solvents facilitated by salting-out effect. The results also revealed that pH has influence on 5-HMF separation with its co-product, especially levulinic acid. Meanwhile, salting-out effect differed depending on the applied solvents. High organic solvent recovery rates indicated its feasibility in industrial application.

1.3 Thesis structure

The objective of this research is to investigate the feasibility of separation and purification of valuable chemicals from hydrothermal conversion product solutions with mixed organic solvents. The innovation herein is that the low boiling point organic solvents are applied, which decrease the energy consumption in further separation. Meanwhile, not only the extraction performance will be studied, but also the effect of extraction conditions will be investigated, including pH and salt concentration.

Chapter 1 of this thesis introduces the research motivation and opportunities.

Chapter 2 is a state-of-the-art review of research in relation to 5-HMF derivatives with their applications, synthesis methods in aqueous solution and other solvents, with or without catalysts, and the technologies for 5-HMF separation and purification. It indicates the existing problems and objectives of the research for this thesis work.

Chapter 3 describes the methodology of this thesis work, which is mainly experimental, including extraction of 5-HMF from simulated HTC product solution and results detection methods, as well as data process methods.

Chapter 4 presents results from the experiments and discussion about extraction and separation performance. It discusses the influence of NaCl concentration and pH level on extraction and purification performance.

Based on the contents in Chapter 4, conclusions and contributions of this work are summarized in Chapter5. In addition, recommendations are made for future work.

Chapter 2

Literature Review

2.1 Derivatives of 5-HMF and their application

There are two functional groups in 5-HMF, hydroxyl group and formyl group (shown in Figure 2-1). The furan ring itself is also a reactive structure. With these features, 5-HMF is able to undergo reduction, oxidation, esterification and many other reactions. These possible reactions endue 5-HMF its versatile derivatives and applications.

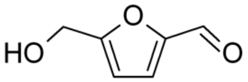

Figure 2-1. Structure of 5-(hydroxymethyl) furfural (5-HMF)

2.1.1 Oxidation of 5-HMF

The hydroxyl group in 5-HMF can be oxidized into an aldehyde or carboxyl group and the aldehyde can be oxidized into a carboxyl group. 5-HMF can undergo a selective oxidation reaction under different conditions. The products include furan-2,5-dicarboxaldehyde (FDC), 5-hydroxymethylfuran-2-carboxylic acid (HFCA), 5-formylfuran-2-carboxylic acid (FFCA) and furan-2,5-dicarboxylic acid (FDA).

The oxidation of 5-HMF into FDC was studied by van Deurzen et al. using chloroperoxidase (CPO) as catalyst and hydrogen peroxide as the oxidant. A 92% conversion of 5-HMF and a maximum selectivity of 74% to FDC were achieved under this condition. The reaction pathways and side-products are shown in Figure 2-2 [32]. Moreau et al. investigated oxidation of 5-HMF to FDC in a batch reactor at 363 K with supported V_2O_5/TiO_2 as catalyst and toluene and MIBK as solvents under an air pressure of 1.6MPa [33].

Gorbanev et al. studied the conversion of 5-HMF into FDA using 1wt % Au/TiO_2 as catalyst and a 71% yield was obtained at 30 °C in 18 hours with 20 bar oxygen in basic aqueous solution [34]. It was also found that more intermediate oxidation product, HFCA, was produced compared with FDA when using a lower pressure or a lower concentration of base. Casanova et al. found that with both catalysts of Au-CeO_2 and Au-TiO_2, the optimal conditions to convert 5-HMF into FDA were 130 ℃ and 10 bar air pressure. An over 99 mol% yield was achieved [35].

Carlini et al. worked on synthesis of FDA from 5-HMF based on $VOPO_4 \cdot 2H_2O$ (VOP) [36]. When VOP and N,N-dimethylformamide (DMF) were used at 100 ℃ and room pressure O_2, 8.13 mmol of FDA/(g catalyst) productivity and 95% selectivity were achieved but with a low 5-HMF conversion.

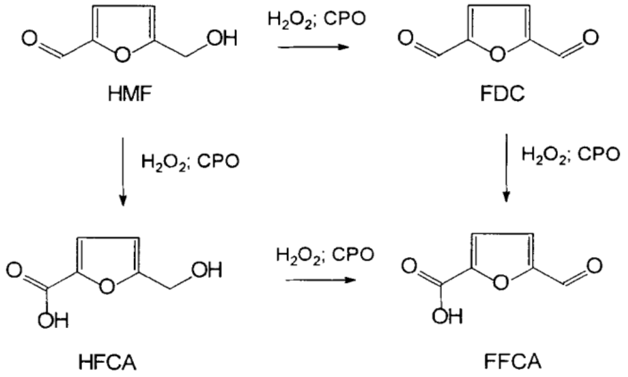

Figure 2-2. Reaction scheme for CPO catalyzed 5-HMF oxidation

2.1.2 Reduction of 5-HMF

Reduction of the formyl group of 5-HMF results in formation of 2,5-bis(hydroxymethyl)furan, which is an important building block for the production of polymers and polyurethane foams [18]. Several researchers reported high yields with nickel, copper chromite, platinum oxide, cobalt oxide, molybdenum oxide and sodium amalgam catalysts [37, 38]. A 100% conversion rate and high selectivity were obtained by using Pt/C, PtO_2 or $2CuO \cdot Cr_2O_3$ [39]. The furan ring was hydrogenated by Pd/C or Raney nickel catalysts to form 2,5-bis (hydroxymethyl) tetrahydrofuran [40].

2.1.3 Other reactions and applications

Esters can be produced via the reaction of alcohol or organic acid with 5-HMF. The product can be used as a fuel, fuel addictive, or a starting materials for the synthesis of monomers for polymerization reactions [7-9].

2-hydroxypropane-1,2,3-tricarboxylate (mumefural, MF), from 5-HMF has shown promising pharmaceutical applications [3]. It is considered as a potential anti-influenza chemical. Chuda et al. have proven that both mumefural and 5-HMF can improve blood fluidity [4]. 5-HMF can be converted into an adenosine receptor (A_{2A}) antagonist, which is identified as a highly potent chemical with 100-fold selectivity for the A_{2A} receptor over the A_1 [41]. This compound has a great potential for pharmaceutical applications. Its synthesis pathway is illustrated in Figure 2-3 [16]. Another compound, 5-aminolevulinic acid (DALA), is one of the most valuable derivatives of levulinic acid. For pharmaceutical industry, 5-ALA is also a commonly used photosensitizing drug in photodynamic therapy for skin cancer treatment [42-44]. Meanwhile, it is not only a useful insecticide [45], but also one type of biodegradable herbicide that shows high activity toward dicotyledonous weeds with little influence on monocotyledonous crops [46]. Its major synthesis pathways are shown in Figure 2-4 and Figure 2-5 [44].

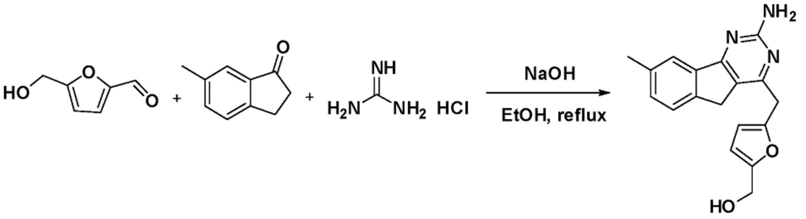

Figure 2-3. Synthesis pathway of adenosine receptor (A_{2A}) antagonist

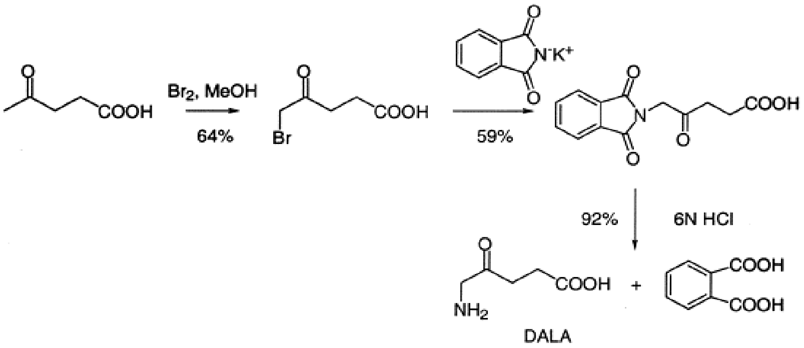

Figure 2-4. Conventional synthesis pathway of 5-aminolevulinic acid

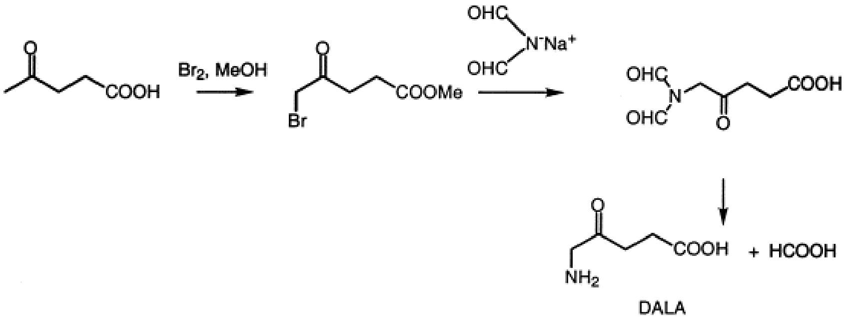

Figure 2-5. NREL synthesis of 5-aminolevulinic acid

Other derivatives are utilized as flavor enhancers in food industry. Terada et al. prepared 5-hydroxymethyl-2-furaldehyde bis-(5-formylfurfuryl) acetal from 5-HMF by using a strong-acid cation-exchange resin as catalyst [6]. The synthesis pathway is shown in Figure 2-6 [16]. The authors reported that 2.3% yield was achieved and indicated its application as flavor-improving agent.

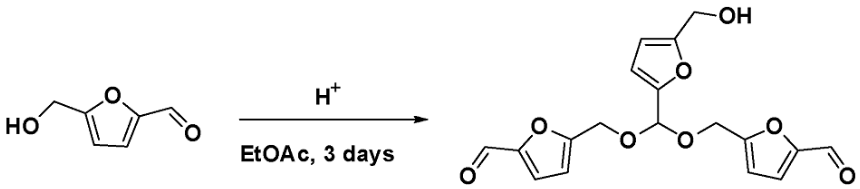

Figure 2-6. Synthesis pathway of 5-hydroxymethyl-2-furaldehyde bis (5-formylfurfuryl) acetal

5-HMF can also react with l-alanine under alkaline conditions to produce N-(1-carboxyethyl)-6-(hydroxymethyl) pyridinium-3-ol, which is also called alapyridaine [5]. Alapyridaine is a new type of flavor enhancer, which is able to enhance several tastes at the same time although it exhibits no flavor itself. Figure 2-7 shows the synthesis pathway of alapyridaine.

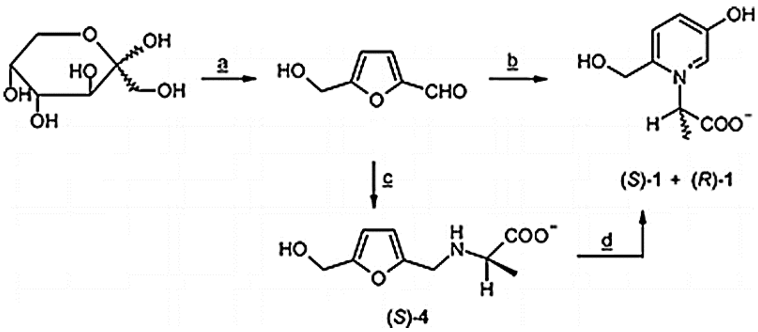

Figure 2-7. Synthesis pathway of taste-enhancer alapyridaine

2.2 Synthesis of 5-HMF

Research on 5-HMF synthesis started in the 1890s, and in 1919, Middendorp published his research on the physical and chemical propertied of 5-HMF as well as its synthesis methods [47]. Since then, it has been updated periodically [39]. The higher concentration and purity of 5-HMF in product solution are beneficial to 5-HMF separation and purification. It was widely accepted that the yield of 5-HMF can be enhanced by using homogeneous or heterogeneous acid catalysts. The synthesis of 5-HMF can be carried out in aqueous solutions and organic solvents as well as ionic liquids. Feedstock conversion rate and 5-HMF selectivity were affected by several factors in reaction, including solvent, catalyst and heating method. The corresponding reaction mechanisms, catalysts, reaction mediates and reaction conditions applied to 5-HMF production are summarized as follows.

2.2.1 Reaction mechanisms

Monosaccharide can be converted into 5-HMF via direct dehydration reaction; for example, one molecule of fructose or glucose loses three molecules of water to form one molecule of 5-HMF. The polysaccharides, such as cellulose, are first decomposed to monosaccharide, which is converted into 5-HMF through further dehydration reaction subsequently. This process is demonstrated in Figure 2-8 [21].

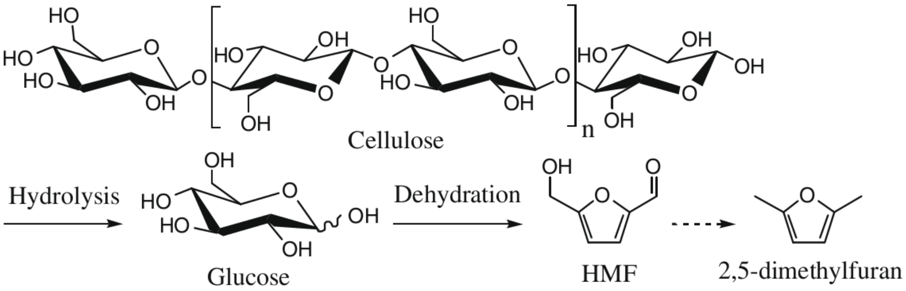

Figure 2-8. Reaction mechanism for cellulose conversion from cellulose into 5-HMF

Different conversion mechanisms of monosaccharide to 5-HMF have been well studied. The formation pathways from D-fructose and sucrose were investigated by Amarasekara et al. [29, 48]. Two conversion pathways are demonstrated in Figure 2-9 [16]. In Pathway A, glucose is transferred into fructose first and then forms the furan ring structure to accomplish the reaction. In Pathway B, glucose does not form furan ring, but is converted into 5-HMF directly through dehydration.

It was reported that glucose with stable ring structure has a lower reactivity than fructose, because the enolization rate of glucose in solution is lower than fructose, which is the rate-determining step for 5-HMF formation [49]. The selectivity of 5-HMF formation is affected by the tautomeric forms of sugar molecule. D-fructose has four tautomeric forms (shown in Figure 2-10), among which the furanoid form exhibits the highest selectivity for 5-HMF formation [50]. Therefore, enhancing the ratio of furanoid form of fructose is one option to increase the selectivity of 5-HMF in reaction. It was found that furanoid form is the dominant existing form of D-fructose in dimethyl sulfoxide (DMSO) [51], and fructose can also be rearranged to the furanoid form in acetone–water mixtures [50]. Therefore, DMSO was adopted as the reaction medium by many researchers.

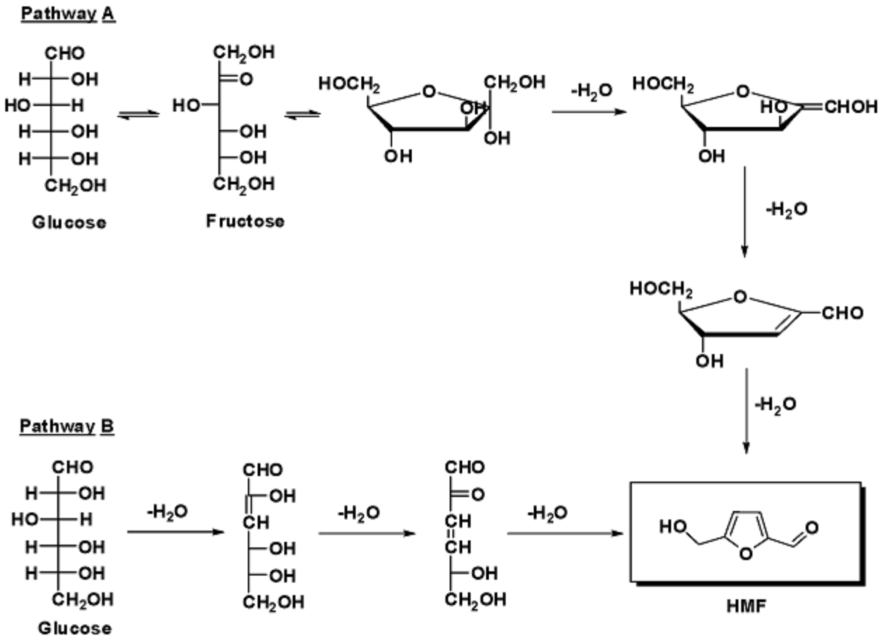

Figure 2-9. Two possible pathways of 5-HMF formation from glucose

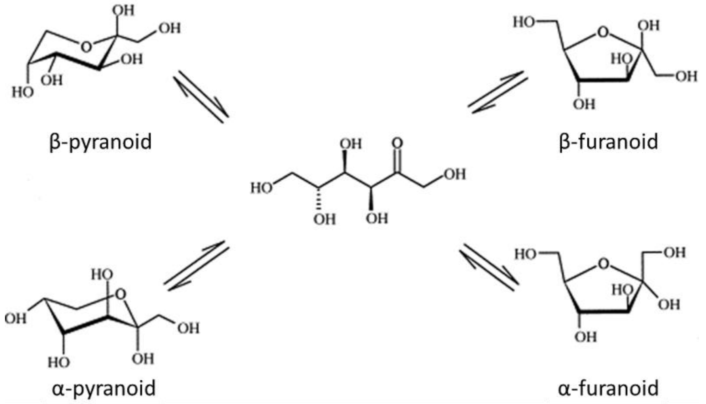

Figure 2-10. Four tautomeric forms of D-fructose

5-HMF undergoes rehydration to form its major co-products, levulinic acid and formic acid, at low pH, but participates in a polymerization reaction between 5-HMF and fructose at high pH [52]. The reaction mechanism is shown in Figure 2-11 [53]. These side-reactions and formation of co-products decreases the 5-HMF yield. Therefore, one of the goals of previous and ongoing researches is to suppress side-reactions and rehydration of 5-HMF in synthesis process.

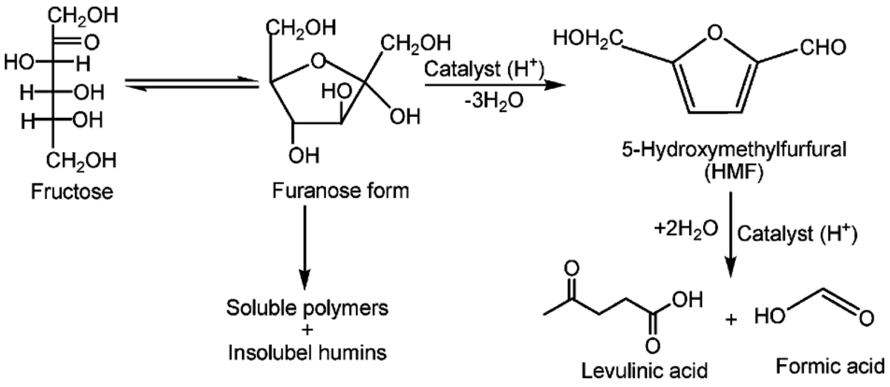

Figure 2-11. Mechanisms of side-reaction and by products formation in 5-HMF synthesis process

2.2.2 Homogeneous catalyst

Both mineral and organic acids can be employed as homogeneous acidic catalysts. The most commonly used mineral acids include HCl, H_2SO_4 and H_3PO_4. It was found that the yield of 5-HMF produced from glucose increased in the order of $H_3PO_4 > H_2SO_4 >$ HCl. Levulinic acid in product increased in the opposite order [54]. The catalytical activities of organic acids, such as citric acid, maleic acid, *p*-toluenesulfonic acid, oxalic acid, were also investigated in subcritical water [55, 56]. It was found that at lower pH (pH=2), phosphoric acid was the favorable catalyst to form 5-HMF, but at relatively higher pH (pH=3), HCl showed a better catalytical activity. In one case, a continuous microreaction process catalyzed by HCl, achieved 54 % yield and 75 % 5-HMF selectivity with 71 % fructose conversion in 1 min [19].

In degradation of fructose or glucose for 5-HMF production, the formation of organic acids decreases the solution pH, which leads to the rehydration of 5-HMF to levulinic acid subsequently. Earlier research has proven that using phosphate buffer solution (PBS) to stabilize pH in reaction was able to address this problem effectively [57]. It was reported that 92% yield of 5-HMF was achieved from glucose and 35% yield from cellulose when using PBS. PBS can be considered as a promising reaction medium for 5-HMF synthesis.

Metal salt, including compounds of chromium, titanium, zirconium and lanthanide, were also used as homogeneous catalyst. When using $CrCl_2$ as catalyst in [EMIM][Cl], 62% yield of 5-HMF was achieved from glucose at 100 ℃ in 3 hours [58]. [EMIM][Cl]–$CrCl_2$ facilitated the isomerization of glucose to fructose, and mechanism is illustrated in Figure 2-12 [59].

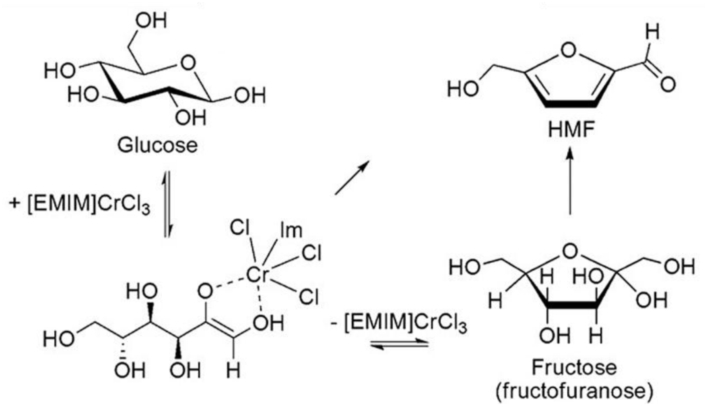

Figure 2-12. Effect of [EMIM] [Cl]–CrCl2 in isomerization of glucose to fructose

The advantages of homogeneous catalysis include that it only involves with one phase operation, which simplifies the reactor design. The homogeneous catalysts also ensure the sufficient and uniform contact of feedstock compounds with catalysts. However, the application of homogeneous acid catalyst causes corrosion of reactor, which implies a great capital cost. Additionally, catalyst recycle and acidic waste disposal remain problems for a homogeneous process.

2.2.3 Heterogeneous catalyst

Recently, many researchers focused on heterogeneous catalysts for 5-HMF synthesis. The advantages of using heterogeneous catalyst include that its separation from aqueous product is much simpler than homogeneous process. Some solid catalysts enable reactions to take place under relatively mild conditions with lower temperatures. These features reduce the corrosion of reactor, and benefit the cost and energy saving.

Moreau et al. studied H-form mordenites and H-form zeolites, which were employed as catalysts in a solvent mixture of water and methyl isobutyl ketone. A yield of more than 70% and selectivity of over 90% were achieved at 165 ℃ [60, 61]. Metal oxides are also widely used as catalysts for 5-HMF synthesis. TiO_2, Zirconia (ZrO_2) and zirconium phosphate (ZrP) were effective in hot compressed or subcritical water [62, 63]. They were able to suppress rehydration of 5-HMF. TiO_2 (A) and ZrO_2 promoted the isomerization of glucose into fructose, while TiO_2 (R) did not have this effect [64]. Sulfated zirconia, prepared from impregnation of ZrO_2 with H_2SO_4, was applied to 5-HMF synthesis in both aqueous and acetone-DMSO mixture solvents. Fructose conversion rate of 93.6% with 5-HMF yield of 72.8% were achieved at 180 ℃ for 20 min reaction time in acetone-DMSO mixture [65]. One modified metal oxide catalyst, hydrated niobium pentoxide ($Nb_2O_5 \bullet nH_2O_2$), converted fructose and inulin to 5-HMF at 160 ℃ in water-2-butanol biphasic system with yields of 89% and 54%, respectively [66].

Besides inorganic catalyst, a carbon-based organic solid acid, which was prepared by a facile and eco-friendly approach from glucose and p-toluene sulfonic acid (TsOH) [67], was used to catalyze fructose dehydration into 5-hydroxymethylfurfural. A 5-HMF yield of 91.2% was achieved in DMSO at 130 ℃ in 1.5 hours. This result is better than those using other catalysts, including Amberlyst-15 AC-SO_3H and zeolite H-BEA under the same conditions. In addition, TsOH can be reused for several times only with minor decline in performance. However, this catalyst was not favorable in an aqueous condition, and gave only a conversion rate of 67%, a selectivity of 12% and a yield of 8%. Another disadvantage of this catalytical process is the utilization of DMSO as solvent, which has negative impact on cost and the environment.

In addition to solid acid catalysts, basic catalysts were utilized in 5-HMF synthesis as well. It has been proven that using a combination of solid acid and base catalysts provided better performance in 5-HMF synthesis at temperatures below 100 ℃. In this process, hydrotalcite promoted the isomerization of glucose to fructose as base catalyst, and Amberlyst-15 catalyzed dehydration of fructose to 5-HMF. The catalysis scheme is shown in Figure 2-13 [68].

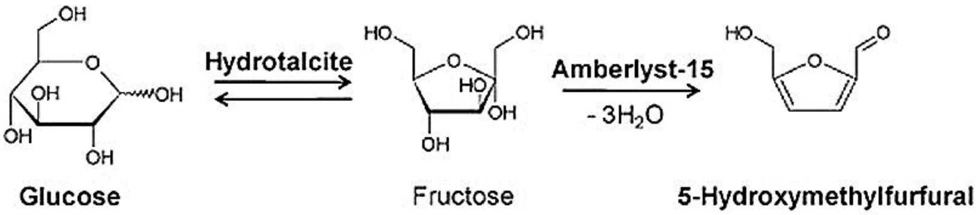

Figure 2-13. Synthesis of 5-HMF from glucose with Amberlyst-15 and hydrotalcite as catalysts

Other complex compounds were also synthesized and employed in 5-HMF production. The application of supported ionic liquid on nanoparticles as catalyst resulted in a fructose conversion rate of 99.9% and a 5-HMF yield of 63% in DMSO at 130 ℃ in 30 min [53]. Micellar heteropolyacid (HPA) catalyst, $Cr[(DS)H_2PW_{12}O_{40}]_3$ was used to convert cellulose to 5-HMF, and a conversion rate of 77.1% and a yield of 52.7% were achieved within 2 h at 150 ℃ [25]. These catalysts all exhibited high stability in recycle.

2.2.4 Synthesis in aqueous solution

The chemical reaction carried out in pressurized hot water with or without catalyst is defined as hydrothermal conversion (HTC), in which the operating temperature commonly ranges from 250 to 450 ℃ [57]. The application of HTC in 5-HMF production has several advantages. First, commonly used feedstock, such as glucose and fructose, has much greater solubility in water than in other organic solvents. This means that a high concentration of feedstock can be processed. Dumesic et al. researched on 5-HMF synthesis from 30wt% fructose solution, and 83% HMF selectivity was achieved [69]. Second, using water as a medium is not only environmentally friendly, but also profitable, because it reduces the cost of solvent. Third, the pressurized hot water is able to provide catalytical condition for 5-HMF formation. It has been reported that dehydration of glucose or fructose is catalyzed by acid catalyst, including mineral acids [56, 70-72] and solid acids [51, 73, 74]. Most researchers agreed that the unique properties of water at high temperatures and high pressures play a significant role in hydrothermal conversion of biomass. Hot water can catalyze both acidic and basic reactions by enhanced self-dissociation of H_2O to H^+ and OH^- [75]. At room temperature, the ionic product for water $K_w = [H+][OH^-]$, is about 10^{-14}, but it increases to 10^{-11} at 200-300 ^oC [76]. This dissociation feature of compressed hot water is favorable for 5-HMF production.

2.2.5 Synthesis with other solvents

Application of organic solvents in 5-HMF production can improve the yield of 5-HMF. The most commonly used organic solvents can be clarified into two categories. Some are miscible with water and act as the co-solvents or modifiers of reaction solution, such as DMSO. Others are not soluble in water or can be salted out to form biphasic system to facilitate extraction of 5-HMF from aqueous solution, such as MIBK, dichloromethane (DCM), tetrahydrofuran (THF), 1- and 2-butanol (this case will be elaborated in 2.3.1).

DMSO is the most favorable co-solvent for 5-HMF production for two reasons. First, it can prevent the formation of co-products such as levulinic acid and humins [18]. Second, since higher ratio of D-fructose molecules exist as its furanoid form in DMSO than in water [77], both higher feedstock conversion and selectivity of 5-HMF were obtained in DMSO [19, 24, 78]. The mechanism of dehydration of D-fructose to 5-hydroxymethylfurfural in DMSO is shown in Figure 2-14, in which DMSO forms intermediate ((4R,5R)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde) with fructose during reaction [48]. 5-HMF produced from D-fructose achieved 92% yield in DMSO at 150 ℃ for 2 hours [72]. A conversion rate of more than 98% and 85% selectivity were achieved by using HCl as catalyst with MIBK-2-butanol or DCM simultaneously extraction with DMSO as co-solvent [79]. The disadvantage of using DSMO as co-solvent is the existence of DMSO in organic phase challenges further purification of 5-HMF. Also, toxic by-products can be generated from the decomposition of DMSO [18].

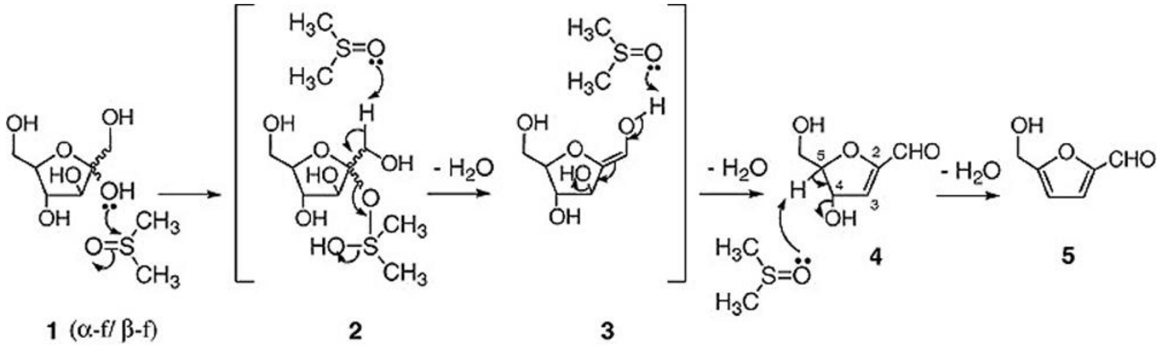

Figure 2-14. Proposed mechanism for the dehydration of D-fructose to 5-HMF

Ionic liquids, known as "green solvents", are a new type of solvent applied to many synthesis reactions. It has several such special properties such as low melting point, suitable viscosity as reaction solvent, and high solubility of polar compounds and other solvents in it. The ionic liquids applied to 5-HMF synthesis include [BMIM]Cl [20, 21], [EMIM][Cl] [59], [ASBI][Tf] [80], [HMIM]Cl [23], [NMM][CH_3SO_3] [81], and [BMIM][BF_4] [22]. Ionic liquids from biorenewable materials, such as choline chloride (ChoCl)-based ionic liquids, were utilized together with low molecule weight organic acid as catalyst as well [27].

DCM and DMSO added in an ionic liquid reaction system can modify the viscosity of ionic liquid to allow easy stirring. Other solvents added in an ionic liquid can realize the extraction of product to suppress the side-reactions of 5-HMF in water; this family of solvents include MIBK, toluene and diethyl ether [27, 82, 83]. Ionic liquids are immiscible with many organic solvent, and this feature makes the extraction and product separation much easier than those in water.

2.2.6 Effect of microwave heating

Microwave irradiation has been widely used in chemical synthesis, which is featured by its high heating speed for reaction system and special effect on reaction results [84]. It can promote 5-HMF formation in a HTC process. Compared with conventional heating methods, microwave heating can increase saccharide conversion, selectivity and yield of 5-HMF, with reduced reaction time. It was reported that 5-HMF was generated in milk and juice during microwave heating [85, 86]. Highly concentrated aqueous fructose (27wt %) was converted to 5-HMF by microwave heating at 200 ℃, and a 53% yield of 5-HMF and 95% conversion of fructose were achieved in 60s with HCl as catalyst. It was also found that the power input of microwave heating changed neither conversion nor product distribution [87].

Microwave heating can be coupled with solid acidic catalysts or ionic liquid as reaction media. Using ionic liquid [BMIM][Cl] as a solvent and $CrCl_3$ as a catalyst, the conversion of fructose, glucose, sucrose, cellobiose and cellulose to 5-HMF with microwave heating was studied [88]. A 5-HMF yield of 71 % was achieved for glucose in 30 s at 140 °C, and 54 % was obtained for cellulose conversion at 150 °C in 10 min. Xylan, corn stalk, rice straw and pine wood were also able to be catalyzed to 5-HMF by $CrCl_3$ in ionic liquid facilitated by microwave heating [20]. Qi et al. applied sulfated zirconia and a strong acidic cation-exchange resin (DOWEX 50WX8-100) as catalyst to convert D-glucose and fructose into 5-HMF with microwave heating in a 70:30 (w/w) acetone/DMSO solvent [89]. With ion exchange resin as catalyst, 97.9% glucose conversion and 91.7% 5-HMF selectivity were achieved in 20 min at 150 ℃. H-form zeolites as solid acid was used to catalyze the hydrolysis of cellulose in ionic liquid (*N*-methyl imidazole) with microwave heating and the reported 5-HMF yield was up to 40% [90].

2.3 Separation and purification of 5-HMF

2.3.1 Solvent extraction theory

Solvent extraction is one of the most favorable separation procedures in chemical industry due to its simplicity. The principle of solvent extraction is the distribution of solutes between two immiscible liquids or phases, which are common to aqueous solutions and organic solvents. The result of solvent extraction is that the solutes are removed from one phase to another phase with being concentrated or separated from other compounds to accomplish the purification. Solvent extraction can be carried out under different conditions ranging from ambient conditions to critical conditions.

Solvent extraction also involves with solvation and solvent-solute interactions. Some liquid properties are influential on solvent extraction procedure, including viscosity, surface tension, vapor pressure, density, polarity (electronegativity, dipole- moment) and polarization ability [91]. Polarity is one of the important properties which affect a solvent extraction process.

According to their permanent dipole-moment, solvents can be classified into polar and non-polar solvents. Polar solvents are favorable for polar compounds extraction, and correspondingly non-polar solvents are favorable for non-polar or low-polar compounds extraction.

Cohesive forces, including dispersion force, Vander Waals force, dipole force and hydrogen bonding, keep liquid molecules together and determine the interactions between molecules.

The square of solubility parameter of liquid (δ) can be expressed as [91]

$$\delta^2 = \frac{\Delta H - RT}{V} \qquad (1)$$

where ΔH -the molar heat of vaporazation;

R - gas constant;

T - thermodynamic temperature;

V - the liquid volume.

Hansen solubility parameter denoted as δ^2 is related to several factors which affect the solvent extraction[91].

$$\delta_{total}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

where δ_d- the energy from dispersion forces between molecules;

δ_p- the energy from dipolar intermolecular force between molecules;

δ_h- the energy from hydrogen bonds between molecules.

According to Eq. (2), dispersion forces, dipolar force and hydrogen bond interaction between molecules are the dominating factors which influence the solvent extraction result. Hansen solubility parameter can be plotted in a three-dimensional space, using δ_d, δ_p and δ_h as axis, called Hansen space. The rule is that two molecules are more likely to dissolve into each other with nearer locations in Hansen space.

2.3.2 Salting-out effect

Salting-out effect refers to the phenomenon that the solubility of certain solute decreases with high concentration of salt present in solution. Salting-out effect can be employed for several applications. It can accomplish phase separation of miscible solvent with water solution. It can also facilitate the extraction of metal-chelates, ion-pairs, or organic materials from solution [92].

Several mechanisms of salting-out effect have been proposed. It was found that the aqueous solubility of a nonelectrolyte dependents on the type of salt and its concentration in solution. The salting-out effect can be evaluated using the Setschenow Equation [93].

$$\log(S/S_0) = -K_{salt}C_{salt} \tag{3}$$

where S - the solubility of the organic solute in aqueous salt solution;

S_0- the solubility of the organic solute in water;

C_{salt} - the molar concentration of electrolyte;

K_{salt} - the empirical Setschenow constant.

The estimation of K_{salt} in Setschenow equation has been developed by several researchers [94-96]. K_{salt} was found to be a function of the intrinsic solubility (S_0) of solute [97]. Xie et al. showed that K_{salt} was determined with Eq. (4)

$$K_{salt} = 0.0018\, V_{LeBas} \tag{4}$$

where V_{LeBas} is the molar volume calculated by the method of Le Bas [98, 99].

NaCl effect on nonelectrolyte solubility in solution was also predicted with another simple equation[100].,

$$K_{salt} = 0.039 log K_{\mathrm{ow}} + 0.117 \tag{5}$$

Different ions display different “salting-out” capacities. It was found that stronger “salting-out” effect could be achieved from anions with double charges [101, 102].

Although 5-HMF and furfural have no dissociable functional group in their structures, their extraction is affected by salt concentration, because salt ions are assumed to bind with water molecules according to ion hydration theory [103]. The distribution of organic solute depends on its interactions with two phases, and the binding of salt ions with water molecules affects the solvation of solutes in aqueous solution, which influences the extraction performance.

2.3.3 Solvent extraction of 5-HMF

Solvent extraction is currently the most popular approach to 5-HMF extraction. Organic solvents can be applied to form biphasic system during reaction, in which 5-HMF can be extracted continuously into the organic phase spontaneously during formation. This process prevents further rehydration of 5-HMF into levulinic acid in aqueous phase. Organic solvents can also be added in after reaction to carry out the extraction of 5-HMF.

It has been proven that ketones or alcohols with 4-C chain were effective in 5-HMF extraction from aqueous product solution [69, 72]. The problem is that, with high polarity, 5-HMF cannot be distributed easily into the organic phase, and it tends to be retained in the aqueous phase. Without modification of the extraction system, the distribution of 5-HMF from aqueous phase to organic phase is not satisfactory. A 5-HMF partition coefficient of only 1.89 was achieved when 30% fructose aqueous solution was catalyzed by H_3PO_4 with MIBK/2-butanol (7:3) as the extraction agent [72]. The partition coefficient (P) was defined as the ratio of solute concentration in organic phase to that in aqueous phase.

By taking advantage of the salting-out effect, salts were introduced into solvents to improve 5-HMF extraction. Salt concentration affects the interaction between solutes or solvents and water molecules [100, 104]. The distribution of 5-HMF between organic and aqueous phases can be improved dramatically in biphasic production system modified with inorganic salt [69, 105]. NaCl and KCl were found to be the most effective to improve both 5-HMF production and extraction. A 5-HMF partition coefficient of 7.3 was obtained when the reaction was carried out in NaCl-saturated biphasic system using THF as extract agent [69]. The result of Dumesic’s research supported this conclusion. With 1-butanol as extract agent, Na_2SO_4 gave the highest partition coefficient of 8.1 for 5-HMF among all salt-saturated biphasic system, which is five times higher than the result from non-salt system [69]. The disadvantage was that the salt may be brought into the organic phase, and more salt is present in the organic phase when a higher salt concentration is used in extraction.

Another challenge to solvent extraction is the separation of 5-HMF from other co-products, or purification of 5-HMF. Two major co-products in 5-HMF synthesis are levulinic acid (LVA) and furfural (FF) [106]. Due to similar properties of 5-HMF and levulinic acid, it is difficult to separate them from each other. Furthermore, furfural can be more easily extracted than 5-HMF and levulinic acid. A 91% furfural recovery rate was achieved by 7:3 (w/w) MIBK:2-butanol from reaction mixture in water-DMSO solution [78].

2.3.4 Other 5-HMF separation methods

Vacuum distillation for liquid separation was patented in 1965; it can be employed for 5-HMF separation since the formation of levulinic acid with acid catalyst makes the direct evaporation or distillation less efficient for its separation from the product mixture. By vacuum distillation, 5-HMF with a concentration of 77.9% produced from acid-catalysis was diluted by polyethylene glycol (Carbowx 600), vacuum dried at 30-35 ℃, and pH 7.6 with a pressure of 1-2 mm. The purity of 5-HMF produced after distillation was reported to be 100% [107].

Supercritical carbon dioxide has been widely used in food industry, biological and environmental research, due to its non-toxic, no-residual and easy separation from the target product [108-110]. Non-function resin was also used for purification of 5-HMF from its synthesis mixture; and a purity of more than 99% was reported[30]. The disadvantage of this method is its reliance on cation exchange chromatography and relatively complex operation. In Vinke’s research, 5-HMF was selectively adsorbed onto activated carbon with loadings up to 30% (w/w) [31]. The use of active carbon prevented the formation of levulinic acid. After absorption, 5-HMF was recovered by extraction of the loaded activated carbon with organic solvents.

2.4 Existing problems

As mentioned above, 5-HMF can be produced by HTC with water as a reaction medium. The aqueous products are composed of 5-HMF, levulinic acid, furfural, organic acids and many other compounds. The technical challenges include not only the improvement of feedstock conversion and 5-HMF formation selectivity in reaction, but also the separation and purification of 5-HMF from the aqueous product. The former has been extensively investigated and several outstanding results have been reported. The latter is the subject of this thesis work because the separation and purification is still a challenge to the HTC technique.

In HTC, it is difficult to achieve both high feedstock conversion rate and 5-HMF selectivity at the same time without any modification or catalyst in reaction system. Although 100% selectivity was achieved by using niobium based catalysts in 6 wt% fructose water solution, only 28.8% fructose conversion was achieved [111]. Similar results were obtained by using zirconium and titanium as catalysts: 99.8% 5-HMF selectivity was achieved, but with only 44.4% fructose conversion rate [112]. It was found that small scale reaction improved the production performance in aqueous solution.

When using microreactor with HCl as catalyst, the convention of fructose was raised to more than 95%, but the selectivity of 5-HMF was sacrificed, which was no more than 60%. The limitation for microreactor is that the glass reactor is too fragile to be built in industry [19]. Also, another drawback is that the industrial level microwave equipment requires high capital, operating, and maintenance costs [113].

Since the concentration and purity of 5-HMF in HTC product solution is not satisfactory, some research focuses on its separation and purification to address the problem. After production, there are two optional measures to process the 5-HMF product mixture. One optional method is conversion of 5-HMF into its derivatives in product mixture first and then separate and purify its derivatives instead of 5-HMF. The critical point is to find certain derivatives which can be produced in 5-HMF product mixture directly with practical conditions, and whose separation is easier then 5-HMF itself.

As summaries in Section 2.1, 5-HMF can be oxidized, reduced and converted to more complex compounds. However, one problem with these processes is that most of these reactions are not able to be carried out in one-pot conversion without condition modifications. For example, the major oxidation products, such as FDA, FDC, FFCA and HFCA cannot be produced directly in aqueous product solution, but in either organic solvent or basic aqueous solution. Since the products are aldehydes or acids with high boiling points and polarities, the application of high boiling point solvent which facilitate the conversion reaction, such as MIBK, still raised the difficulty for its purification. The synthesis of reduction products involves the precious metal such as Pd, or Pt in catalyst preparation, which increases the cost greatly. Meanwhile, the problems of catalytic activity loss or catalyst leaching in aqueous solution should be considered as well in many reactions. The ester and ether formation and separation direct from 5-HMF product mixture have been reported successful for polymer production. However, the major problem for this conversion process is the significant decrease of the product market value.

For some applications, high purity of 5-HMF is required, such as in production of medicines or additives in food industry. If the further synthesis reaction is carried out directly in product mixture without purification, complex side reactions will cause the formation of many undesired by-products, which make the further separation more difficult and increase the consumption of reactants. Therefore, the separation of 5-HMF from its product mixture instead of its derivatives is necessary in some cases.

Homogeneous catalytic reactions with inorganic acids are the most economic methods for 5-HMF production. However, the inorganic acidic catalysts are difficult to be recycled, and they may catalyze the rehydration of 5-HMF into levulinic acid in subsequent separation process. The application of acidic solution also results in the equipment corrosion. Although PBS, as one of the homogeneous acidic catalysts, increases the purity of 5-HMF in product solution, it introduces the emulsification of organic solvents in extraction easily, which causes difficulty for further separation.

Among heterogeneous catalysts, some solid acidic catalysts are only applicable in organic solvents, but not favorable in aqueous solution. For example, functional resins, as the effective catalysts for 5-HMF synthesis, are not resistant to high temperature. This disadvantage prolongs the reaction time to hours.

Using ionic liquids as reaction media results in less environmental impact and less solvent residue in product. But some of them are not applicable to biphasic reaction system, since organic solvents such as glycerol, which lower the dielectric constant, cause the catalytical activity loss of ionic liquid. DMSO is another favorable reaction medium for 5-HMF production. It requires the application of vacuum distillation to accomplish its separation with products, which is energy consuming.

The non-polar property limits the application of supercritical CO_2 to 5-HMF extraction, which is more favorable for non-polar or low polar compounds extraction instead of polar compounds [114]. Modifier can improve its extraction performance for 5-HMF from solid samples [115]. The problem is that commonly used modifiers, such as ethanol and methanol, however, are not applicable to 5-HMF extraction from aqueous solutions due to their low distribution coefficient between supercritical carbon dioxide and water [116]. When these modifiers contact with water, they are released from CO_2 and dissolved in water, and lose their abilities to facilitate the extraction. Therefore, modifiers are applicable in organic compound extraction from solid sample, but not for extraction from aqueous solution. For adsorption using non-function resin or active carbon, the major problem is that the complete desorption is difficult to be achieved, which hinder its application in industry.

Although organic solvent extraction has the disadvantages including environmental impact, requirement of distillation for separation, and slightly increased cost, it is still one of the most practical and feasible processes for 5-HMF separation. It can be carried out in biphasic sytem spontaniously with the reaction, and it requires neither extra catalysts nor high capital investment. However, most researchers reported the partition coefficient or recovery rate of 5-HMF in extraction, while few have reported the separation results of 5-HMF from those co-products.

In addition, extraction and separation conditions exert influence on 5-HMF extraction, including pH, salting-out effect in extraction system. Since as a weak organic acid, the existing forms of levulinic acid are expected to be determined by pH level. Molecules with different existing forms behave distinctively when distributing between the aqueous and organic phase. Thus, pH condition could have influence on levulinic acid extraction and separation. Since "salting-out" effect has a significant influence on organic solvent extraction. Although 5-HMF and furfural have no dissociable functional group in their structures, their extraction is affected by salt concentration, because salt ions are assumed to bind with water molecules according to ion hydration theory [103]. The distribution of organic solute depends on its interactions with two phases, and the binding of salt ions with water molecules affects the solvation of solutes in aqueous solution, which influences the extraction performance. Meanwhile, the possibilities of recycle and reuse of the mixed solvents is one the major concerns of applications to evaluate its feasibility in industry. It requires more research. However, no research focused on these aspects was carried out specifically.

Different from single solvents, the properties of mixed solvents, such as polarity and solubility in aqueous solution, can be adjusted by solvent mixing. The extraction performance is affected strongly by these properties. Mixed solvents have been applied in components extraction from coal or other samples to improve the extraction performance [117]. Herein, mixed solvents will be applied to 5-HMF extraction from its simulated product mixture with different conditions.

2.5 Research objectives

This research investigate the separation and purification of 5-HMF from its simulated product solution with its co-product of levulinic acid and furfural using mixed solvent extraction. The objectives are designed as followed.

1) The separation and purification of 5-HMF from simulated product solution with levulinic acid and furfural as co-product in mixed solvents extraction will be evaluated by comparing with the results of single solvent extractions.

2) The pH effects on 5-HMF extraction and separation will be studied by analyzing the results from different pH levels.

3) Different salt concentrations will be tested to reveal the relationship between salt concentration and separation efficiency for 5-HMF.

4) The possibilities of recycle and reuse of the mixed solvents will be investigated as one of the criteria to evaluate its feasibility in industry.

Chapter 3
Methodology

3.1 Mixed solvent extraction of 5-HMF from simulated solution

3.1.1 Materials and their properties

All the chemicals in this thesis work were purchased from Sigma-Aldrich. Experiments were carried out using simulated aqueous HTC products by mixing 5-HMF with levulinic acid and furfural at different ratios. Salt was also added into the system to facilitate the extraction. The solute concentrations mimicked the components in the hydrothermal conversion product from research done by Asghari et al. [56]. Although their results were not the best in 5-HMF production by hydrothermal conversion, it is considered feasible in industrial production due to its simple operation and the readily available catalyst. The compounds in the product from Asghari's reaction in subcritical water are listed in Table 3-1.

Table 3-1. Compounds in product from HTC reaction in subcritical water

Compounds in product	Percentage (%)	Compounds in product	Percentage (%)
5-HMF	65.30	glycol aldehyde	0.73
furfural	3.90	pyruvic acid	1.40
fructose	2.08	formic acid	3.06
glucose	0.39	acetic acid	1.72
erythrose	0.45	levulinic acid	N/A*

* Levulinic acid was not detected in product.

As shown in Table 3-1, 5-HMF and furfural were major compounds in the product. However, levulinic acid was added in my simulated solution since it most likely exists in most HTC products, although at a low quantity. The concentrations of 5-HMF in sample solution varied from 3.59% to 5.37%, levulinic acid concentrations from 0.35% to 0.56% and furfural concentration from 0.57% to 0.74%. Within these ranges of concentrations, the solutes dissolved in organic solvent did not change the properties of organic phase greatly. Therefore, the partition of solutes between two phases could be considered independent of solute concentrations.

The applied organic solvents were DCM, 2-butanol and THF. The properties of DCM, 2-butanol and THF were listed in Table 3-2. DCM is a commonly used organic solvent for the production of 5-HMF and levulinic acid [72, 74, 118]. 2-butanol has been proven effective for 5-HMF production and extraction in biphasic systems [19, 78, 119]. THF is less toxic than DCM. THF exhibited a promising extraction potential for 5-HMF [69]. All these solvents have boiling points lower than 100 ℃ and low enthalpy of vaporization, which means less energy consumption during solvent recycle by evaporation.

Table 3-2. Properties of DCM, 2-butanol and THF

Solvent	Enthalpy of vaporization （kJ/mol)	Polarity index	Boiling point (at 760 mmHg)	Vapour Pressure (mmHg at 25 ℃)	Density at 25 ℃ (g/cm^3)	Solubility in water at 25 ℃ (g/L)
THF	29.81	4.2	68.278	152.44	0.904	miscible
2-butanol	40.75	4.0	96.608	25.24	0.802	181
DCM	28.06	3.4	39.639	448.01	1.252	13

Polarity index is adopted herein to estimate solvent polarity in bulk extraction, which is the parameter indicating the interaction between solvent and various polar test solutes [120].

3.1.2 Mixed solvent extraction

Three groups of mixed solvents used in this work and the corresponding ingredients are listed in Table 3-3. Mixed solvents are the mixtures of DCM and THF (Group 1), DCM and 2-butanol (Group 2), and THF and 2-butanol (Group 3), and the individual solvents are DCM, 2-butanol and THF.

Considering a mixed solvent made up of organic solvents A and B, their polarity indices are denoted as P'_A and P'_B, and their volume fractions are denoted as x_A and x_B, respectively ($x_A + x_B = 1$). Then the polarity index of the mixture P'_t can be calculated using Eq. (6) [121].

$$P'_t = x_A P'_A + x_B P'_B \qquad (6)$$

Eq. (6) shows that the polarity of a mixed solvent can be adjusted by changing the mixing volumetric ratio of the organic solvents with different polarity indeces.

Table 3-3. Properties of mixed organic solvent in extraction with NaCl

Group No.	Solvent	Entry No.	solvent volume ratio	Estimated polarity index
1	DCM-THF	1	1 : 4	3.98
		2	1 : 1	3.65
		3	4 : 1	3.32
2	DCM - 2-butanol	4	1 : 4	3.74
		5	1 : 1	3.50
		6	4 : 1	3.26
3	2-butanol -THF	7	1 : 4	4.14
		8	1 : 1	4.05
		9	4 : 1	3.96
-	DCM	10	-	3.10
-	2-butanol	11	-	3.90
-	THF	12	-	4.20

It has been reported that pH 2.0 and pH 2.5 were the optimum conditions for 5-HMF production in aqueous solution [56, 122]. Therefore, pH 2.0 and pH 2.4 were tested herein. The pH of sample solution was adjusted by HCl, and it was measured by a pH meter (Oakton 700) with a resolution of pH 0.01.

The sample solution was modified with 10 wt% and 20 wt% NaCl. Preliminary tests were carried out to determine the applicable NaCl concentration. 5wt%, 10wt%, 15wt%, 20wt% and 25wt% NaCl aqueous solutions were tested in biphasic system for all solvent combinations. These tests showed that 10wt% NaCl was the minimum concentration that enabled phase separation rapidly for all extraction mixtures. When 25wt% NaCl solution was mixed with organic solvent, NaCl precipitated out from solution. Therefore, no more than 20wt% NaCl was applied in my study herein.

Liquid-liquid extraction was carried out in a 20 mL glass vial. 2.5 mL mixed organic solvent was mixed with 2.5 mL aqueous sample solution, and then the vial was shaken manually for 3 minutes. Then the mixture was left still in separatory funnel for 30min to enable the phase separation. After phase separation, the volumes of aqueous phase (V_{aq}) and organic phase (V_{org}) were measured with a 10 ml graduated cylinder.

Each experiment data points in this thesis were replicated twice or three times and the mean values are presented.

3.2 Analysis method

The aqueous phase after separation was analyzed using HPLC (Waters 2690) equipped with a Zorbax SBC18 reverse phase column (Agilent). The mobile phase was using a 1:7 (v/v) methanol : H_2SO_4 (0.1mM, pH 2.5) at a flow rate of 1.0 ml/min. The column temperature was set at 303 K. The retention time for levulinic acid, 5-HMF and furfural under this condition were 3.15 min, 3.65 min, and 5.05 min, respectively.

The chromatography was equipped with a PDA detector (Waters 996). The wavelength of UV detector was set at 323, 315 and 254 nm for 5-HMF, furfural and levulinic acid, respectively. External standard method was employed to calibrate HPLC-PDA system. It was carried out with 2 wt% standard aqueous solution of 5-HMF, levulinic acid and furfural by using 5 levels of injection volume. The calibration curve was plotted from peak areas in chromatograms of the standard samples. Component concentrations in aqueous phase after extraction were obtained from this standard curve.

3.3 Data analysis

3.3.1 Extraction performance evaluation

The concentrations of 5-HMF, levulinic acid and furfural in the aqueous phase were used for the calculation of partition coefficient, separation factor, 5-HMF purity and solute recovery rate in the extracted product.

The concentration of 5-HMF in organic phase C_{org} is calculated using Eq. (7).

$$C_{org} = \frac{C_0 \times V_0 - C_{aq} \times V_{aq}}{V_{org}} \tag{7}$$

where V_0 - the initial volume of simulated THC product solution ($V_0 = 2.5mL$);

C_0 - initial concentrations of solute in simulated HTC product solution;

C_{aq} - solute concentration in aqueous phase after extraction;

V_{org} - the volumes of organic phase after extraction;

V_{aq} - the volumes of aqueous phase after extraction.

The partition coefficient (P) was defined as the ratio of solute's concentration in organic phase to that in aqueous phase. A greater P means more solute distributed into the organic phase. In this study, greater partition coefficient of 5-HMF (P_{HMF}) together with lower partition coefficient of levulinic acid (P_{LVA}) and furfural (P_{FF}) are desired; it means more 5-HMF and less levulinic acid or furfural has been extracted from the aqueous phase into the organic phase.

The separation factor was defined as the ratio of partition coefficients of solute A to that of B. For simplicity, the separation factor between 5-HMF and levulinic acid is denoted as S_1 and that between 5-HMF and furfural as S_2. The greater magnitude of S indicates the better separation performance.

Finally, the recovery rate (R) was determined by the ratio of the solute mass extracted out by organic solvent to the initial solute mass in simulated HTC product, as shown in Eq. (8). Recovery rate indicates the portion of solute recovered after solvent extraction. A greater R_{HMF} means a greater portion of 5-HMF recovered from the simulated HTC product.

$$R = \frac{C_{org} \times V_{org}}{C_0 \times V_0} \times 100\% \tag{8}$$

The purity of 5-HMF after extraction, denoted as p, was calculated to evaluate the purification effect. It was defined as the portion of the mass of 5-HMF (M_{HMF}) in total mass of solute (M_{total}), and it was calculated as,

$$p = \frac{M_{HMF}}{M_{total}} = \frac{C_{HMF} \times V_{org}}{C_{HMF} \times V_{org} + C_{LVA} \times V_{org} + C_{FF} \times V_{org}} = \frac{C_{HMF}}{C_{HMF} + C_{LVA} + C_{FF}} \tag{9}$$

in which C_{HMF}, C_{LVA}, and C_{FF} are the concentrations of 5-HMF, levulinic acid and furfural in organic phase after extraction, respectively.

Solvent recovery rate was also quantified, since it is one of the key factors for cost estimation in industry. Solvent recovery rate is defined herein as the ratio of the organic phase volume to the initial organic solvent volume, which is 2.5 mL in all tests.

3.3.2 Mixed solvent performance assessment

To understand how each individual solvent performed in the mixed solvent, the partition coefficients determined from experiments were compared with the calculated theoretical values. The calculation for theoretical values are based on two assumptions, one is that the solute distributions into the organic phase do not interact with each other, and the other is that the organic solvent functioned independently in mixed solvent extraction. For a mixed solvent composed of solvents A and B with volumes V_A and V_B, the mass of the solutes dissolved in solvents A (M_A) and B (M_B) can be calculated with Eq. (10) and (11) .

$$M_A = C_{orgA} \times V_A \tag{10}$$

$$M_B = C_{orgB} \times V_B \tag{11}$$

Where the concentrations of solute in solvent A is denoted as C_{orgA}, and in solvent B as C_{orgB}, respectively. Therefore, the total mass of solute in organic phase (M_{org}) is the sum of mass of solute in solvent A (M_A) and B (M_B), that is

$$M_{org} = M_A + M_B = C_{orgA} \times V_A + C_{orgB} \times V_B \tag{12}$$

The concentration of solute in organic phase C_{org} is determined by total mass of solute in organic phase and total volume of organic phase (V_{org}) which is the sum of V_A and V_B.

The volume concentration of solute in organic phase can be calculated as,

$$C_{org} = \frac{C_{orgA} \times V_A + C_{orgB} \times V_B}{V_A + V_B} \tag{13}$$

Partition coefficients of solute in solvents A (P_A) and B (P_B) in single solvent extraction are defined as,

$$P_A = C_{orgA}/C_{aq} \tag{14}$$

$$P_B = C_{orgB}/C_{aq} \tag{15}$$

The concentration of solute in organic phase was calculated using Eq. (16).

$$C_{org} = \frac{C_{aq}(P_A \times V_A + P_B \times V_B)}{V_A + V_B} = C_{aq}(x_A P_A + x_B P_B) \tag{16}$$

where x_A and x_B were the volume fractions of solvent A and solvent B in mixed solvent, which were calculated with Eq. (17) and (18).

$$x_A = \frac{V_A}{V_A + V_B} \tag{17}$$

$$x_B = \frac{V_B}{V_A + V_B} \tag{18}$$

The theoretical partition coefficient of mixed solvent, denoted as P_0, can be calculated with Eq. (19). It represents the total effect of mixed solvent extraction.

$$P_0 = \frac{C_{org}}{C_{aq}} = x_A P_A + x_B P_B \tag{19}$$

The error bar was added in charts using standard deviation of the sample, denoted by S_N and defined as follows.

$$S_N = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2} \tag{20}$$

where x_i is the observed values of the sample items, $\bar{x}$ is the mean value of sample data, and N is the sample size.

Chapter 4

Results and Discussion

4.1 Extraction and separation using single solvents

All the results from mixed solvent and single solvent extractions are listed in Table 4-1. For easier understanding, some results presented in Figures are taken from this table.

4.1.1 Extraction of 5-HMF

The partition coefficients of 5-HMF in single solvent extraction with 20 wt% NaCl at pH 2.4 are shown in Figure 4-1.The partition coefficients of 5-HMF were affected by solvent polarity, which decreased in the order of DCM < 2-butanol < THF. The general conclusion is that 5-HMF is easier to be extracted by high-polarity solvent from previous studies [123]. The results from single solvent extraction in this experiment agreed with this conclusion. As a non-polar and aprotic solvent, DCM was the least favorable for 5-HMF extraction among these three single solvents. The lowest 5-HMF partition coefficient was obtained in DCM extraction.

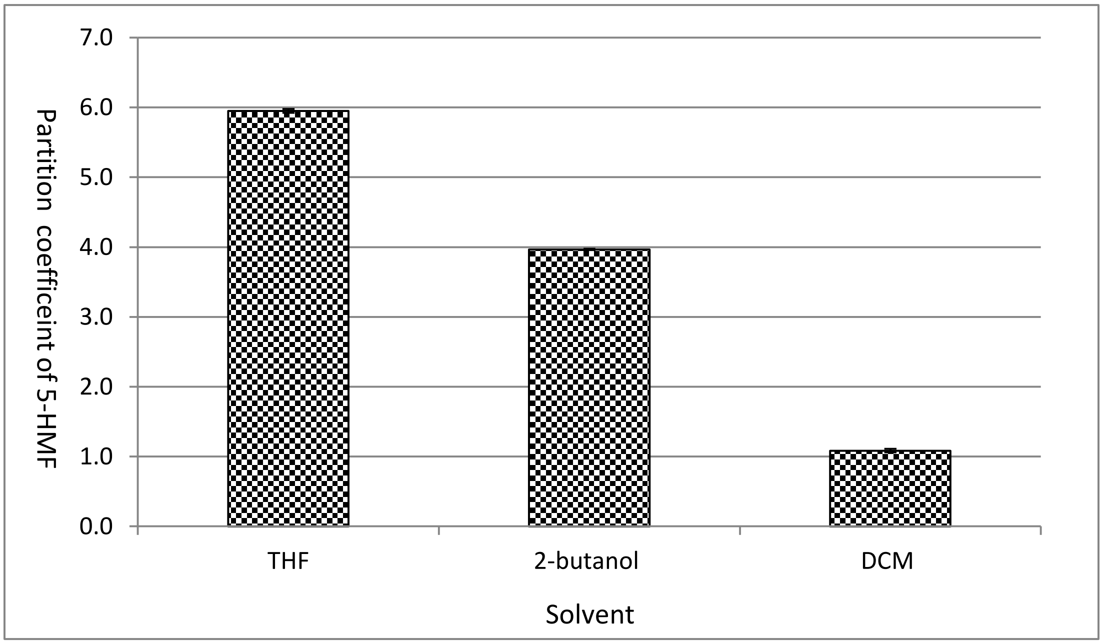

Figure 4-1. P_{HMF} in single solvent extraction with 20wt% NaCl at pH 2.4

Table 4-1. Partition coefficients, separation factors and recovery rates of 5-HMF, LVA and furfural after extraction with 20wt% NaCl at pH 2.4

Group No.	Solvent	Entry Number	P_{HMF}	Stdev of P_{HMF}	P_{LVA}	Stdev of P_{LVA}	P_{FF}	Stdev of P_{FF}	S_1	S_2	R_{HMF} (%)	R_{LVA} (%)	R_{FF} (%)	Purity of 5-HMF (%)
1	DCM-THF	1	4.50	10.1%	2.20	4.4%	15.31	33.6%	2.04	0.29	81.8	68.8	93.9	75.7
		2	3.48	24.4%	1.48	8.1%	17.50	59.7%	2.35	0.20	77.7	59.7	94.6	75.3
		3	2.32	0.2%	0.81	2.9%	22.47	73.0%	2.86	0.10	69.9	44.8	95.7	74.2
2	DCM - 2-butanol	4	5.14	16.5%	3.61	71.9%	11.58	23.5%	1.42	0.44	83.7	78.3	92.1	75.7
		5	6.87	0.1%	3.71	13.7%	22.60	57.6%	1.85	0.30	87.3	78.8	95.8	75.9
		6	3.86	8.0%	2.05	30.8%	26.83	98.1%	1.88	0.14	79.4	67.2	96.4	74.9
3	2-butanol -THF	7	6.87	12.5%	3.69	0.8%	14.53	13.0%	1.86	0.47	87.3	78.7	93.6	76.3
		8	5.48	21.3%	2.87	6.2%	11.24	41.0%	1.91	0.49	84.6	74.2	91.8	76.2
		9	4.06	2.4%	1.61	80.8%	8.13	5.4%	2.52	0.50	80.2	61.7	89.1	76.6
4	DCM	10	5.95	2.8%	3.956	6.6%	14.12	45.4%	1.50	0.42	85.6	79.8	93.4	75.9
5	2-butanol	11	3.965	0.9%	2.90	2.4%	4.98	10.0%	1.37	0.80	79.9	74.4	83.3	76.4
6	THF	12	1.08	2.4%	- 0.22*	0.3%	31.22	128.9%	-	0.03	52.0	-	96.9	-

P_{HMF}, P_{LVA}, P_{FF} - Partition coefficient of 5-HMF, levulinic acid and furfural;

Stdev - Standard deviation ;

S_1 - Separation factors between 5-HMF and LVA;

S_2 - Separation factors between 5-HMF and furfural;

R_{HMF}, R_{LVA}, R_{FF} - Recovery rate of 5-HMF, levulinic acid and furfural.

* This value is negative, which was not taken into calculation for further analysis.

According to the theory of hydrogen bond formation [124], there are at least two possible ways for 5-HMF to form hydrogen bonds. One is involved with the oxygen atom on its furan ring, which is ready to form hydrogen bond with hydrogen donor. The other way is using the hydroxymethyl group in its structure, which can act as hydrogen donor and combine with another hydrogen receiver in organic solvent structure.

THF is proven to be an effective organic solvent for 5-HMF extraction in biphasic reaction system, which was also mentioned in previous research [69]. Its extraction capacity for 5-HMF can be attributed to two different reasons. First, although THF, as an aprotic solvent, cannot act as hydrogen donor, it still can form hydrogen bonds with water molecules via the oxygen atoms in its structure as hydrogen acceptor [125]. This implies the possibility for THF to form hydrogen bonds with the hydroxyl group in 5-HMF, as well as with the carboxyl group in levulinic acid. This interaction between solute and solvent molecules is able to facilitate the migration of 5-HMF and levulinic acid from aqueous phase to organic phase. Second, according to ‘like dissolves like’ rule [126], THF is favorable for 5-HNF extraction due to the furan ring in its structure. The same effect also influenced the extraction of furfural from simulated solution.

For 2-butanol, its interaction with 5-HMF is more complicated, which implied that some interaction other than hydrogen bond between molecules of alcohol solvents and 5-HMF also participated in the extraction process. Due to steric effect, it is usually easier for 1 ° alcohol to form hydrogen bonds than 2 ° alcohol [127]. Therefore, if hydrogen bond were the major interaction between butanol and 5-HMF that affects the extraction performance, then theoretically the partition coefficient of 5-HMF should be greater in extraction with 1 ° alcohol than with 2 ° alcohol. However, the experimental data exhibited otherwise. In Dumesic’s research, 5- HMF achieved greater partition coefficients in extraction with 2 ° alcohols than the corresponding 1 ° alcohols under the same condition [69]. However, the specific reason for this phenomenon requires further investigation in the future.

4.1.2 Extraction of levulinic acid and furfural

Partition coefficients of levulinic acid and furfural in single solvent extractions with 20 wt% NaCl at pH 2.4 are shown in Figure 4-2 and Figure 4-3. The partition coefficients of levulinic acid displayed an obvious correlation with solvent polarity in single solvent extraction, which decreased in the order of THF > 2-butanol > DCM. The interaction of hydrogen bonds between THF and levulinic acid, which facilitated the extraction of levulinic acid by THF (mentioned in section 4.1.1). The relatively high partition coefficients of levulinic acid in extraction of 2-butanol can be attributed to its straight chain structure, which is similar to the structure of levulinic acid. The similarity in their structures is considered the factor that benefited the extraction of levulinic acid.

The partition coefficient of levulinic acid in extraction by DCM was negative. It indicates that the total mass of levulinic acid in aqueous phase after extraction was higher than its initial amount. This result was possibly explained by two possible reasons. One is that the existence of DCM promoted the rehydration of 5-HMF into levulinic acid. However, in simultaneous extraction with DCM, no results indicated that DCM has catalytical activity for rehydration of HMF [78]. Another is that there was certain interaction existing between levulinic acid and DCM, which changed its UV absorption properties. It was most likely to influence its absorption peak during HPLC-UV analysis, which may result in inaccurate measurements of concentrations. However, neither of these two interpretations is able to be explained or verified concretely right now, and this phenomenon still requires further investigation to better understand its mechanism.

The partition coefficient of furfural in single solvent extraction, which decreased in the order of DCM > THF > 2-butanol, did not show a simple correlation with solvent polarity. As mentioned in Section 4.1.1, solute extractions were affected by several factors. With the lowest polarity, DCM was most favorable for furfural extraction among three solvents employed. Although THF has a similar moleculor structure with furfural, it still gave much lower P_{FF} than DCM due to the high polarity of THF. It implied that furfural extraction was affected more by the solvent polarity than the solvent molecular structure. With a high polarity and a straight-chain structure, 2-butanol was the least efficient for furfural extraction in the tests herein.

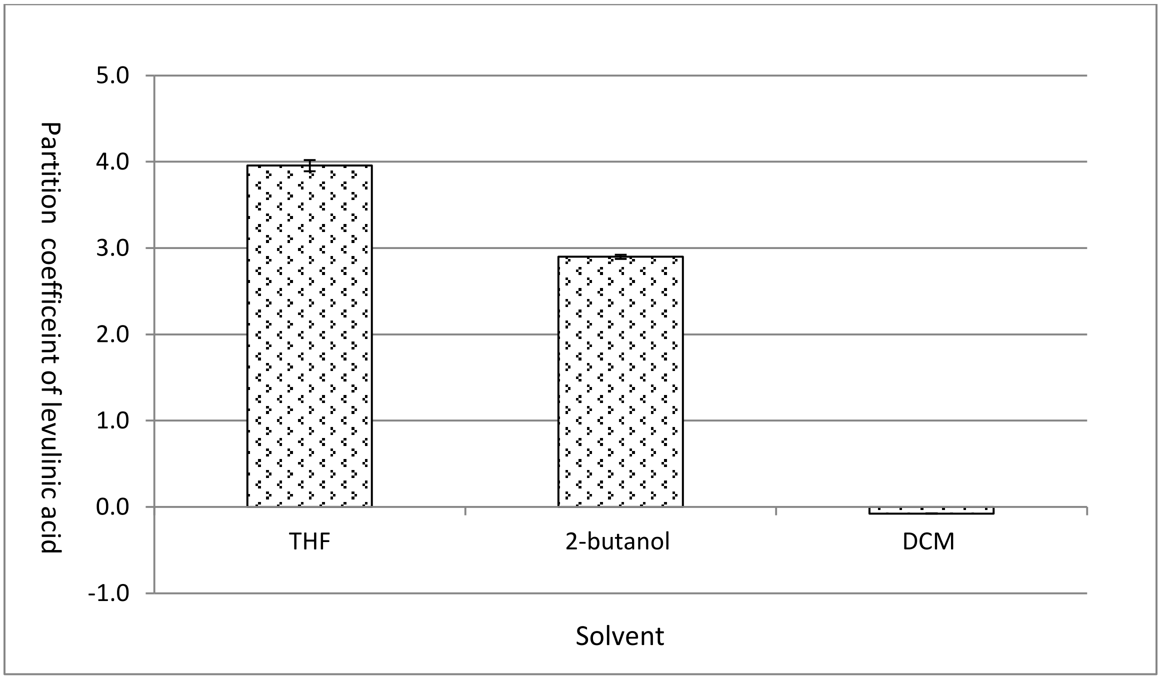

Figure 4-2. P_{LVA} in single solvent extraction with 20wt% NaCl at pH 2.4

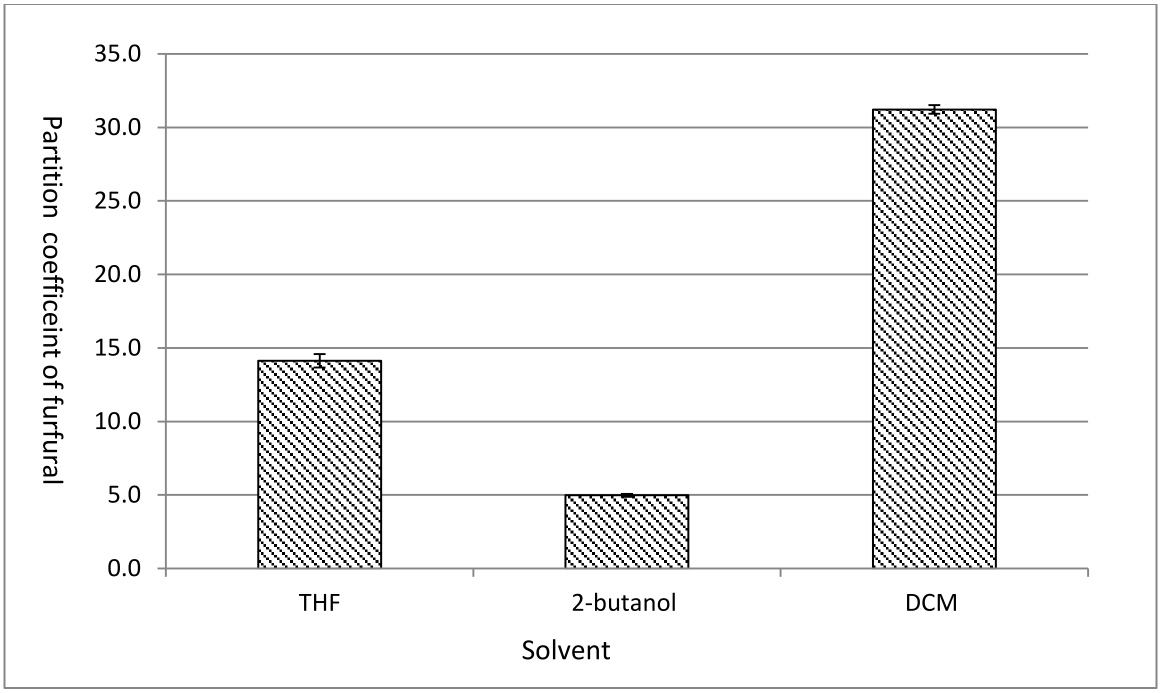

Figure 4-3. P_{FF} in single solvent extraction with 20wt% NaCl at pH 2.4

4.1.3 Separation of 5-HMF with levulinic acid and furfural

The separation performance is based on the partition coefficients of both 5-HMF and its co-products, and results from single solvent extraction are shown in Figure 4-4. The results were calculated from the average partition coefficient of repetitive results, so there is no standard deviation presented.

Although the partition coefficients of 5-HMF and levulinic acid were both highly related to solvent polarity, Figure 4-4 shows the separation factors of 5-HMF and levulinic acid behaved differently along with solvent polarity. Separation factor between 5-HMF and levulinic acid S_1, in extraction by THF was greater than those from extraction by 2-butanol. Since the partition coefficient of levulinic acid was negative in extraction with DCM, its separation factor was ignored. 2-Butanol exhibited lower separation factor between 5-HMF and levulinic acid than THF. The reason is that although 2-butanol has high polarity and hydrogen donor functional group to interact with 5-HMF, its straight chain structure was relatively favorable for levulinic acid extraction compared with 5-HMF.

the separation of 5-HMF with furfural was not able to accomplish with single solvent extraction. The separation factors between 5-HMF and furfural increased in the order of 2-butanol > THF > DCM. However the major problem is that all of the separation factors were less than 1.

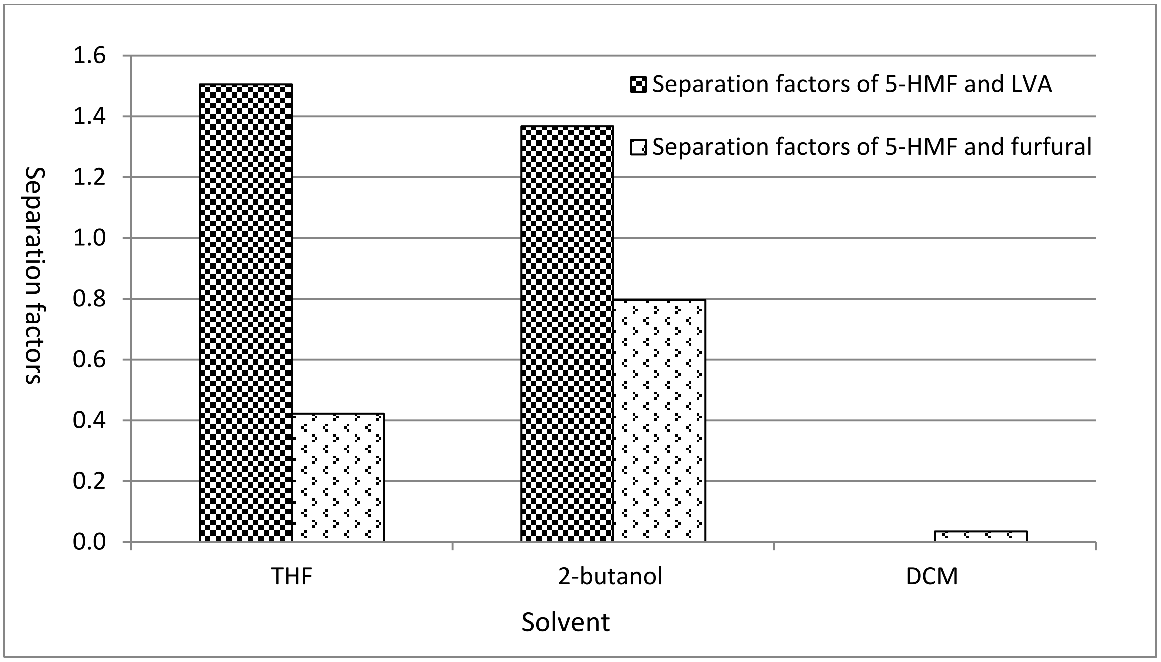

Figure 4-4. Separation factors in single solvent extraction with 20wt% NaCl at pH 2.4

4.2 Extraction and separation with mixed solvents

4.2.1 Extraction of 5-HMF

Partition coefficients of 5-HMF in mixed solvent extraction with 20wt% NaCl at pH 2.4 are shown in Figure 4-5. In mixed solvent extraction with DCM and THF, the partition coefficients of 5-HMF and levulinic acid increased with an increase of polarity, but the separation factors decreased. Similar trend happened in mixed solvent extraction with 2-butanol and THF. This indicated that the application of high polarity solvent did not benefit the separation of 5-HMF and levulinic acid, because high polarity solvents are also effective for the extraction of levulinic acid.

However, the partition coefficients of 5-HMF did not always exhibit the consistency with solvent polarity in mixed solvent extraction. In mixed solvent extraction with DCM and 2-butanol, P_{HMF} and P_{LVA} did not show the simple trend as those in other two groups. Entry 5 with DCM-2-butanol (1:1) showed the highest partition coefficients for both 5-HMF and levulinic acid. With 20wt% NaCl, partition coefficient of 5-HMF were, in Entries 5 and 9, comparable to each other with a value of 6.87 and a recovery rate of 87.3%. Both are higher than the results achieved by each single solvent extraction. With 10wt% NaCl, the highest P_{HMF} (4.49) and levulinic acid (2.35) corresponded to Entry 5 (refer to Table 4-1). The highest partition coefficient of 5-HMF (6.87) achieved was not as high as that reported by Dumesic et al. (7.3) in extraction using THF with saturated NaCl [69]. This can be attributed to the difference in operating conditions including pH, NaCl concentration and extraction temperature. Dumesic et al. carried out 5-HMF extraction during reaction at the temperature of 180 ℃, whereas this experiment was conducted at room temperature. The effect of temperature on extraction varies for different solutes according to their properties, as well as extraction process features, which can be entropy or enthalpy driven process, endothermic or exothermic process. For example, the extraction of some sulfonamides is an enthalpy driving process, and their n-octanol/water partition coefficient decreased with an increase in temperature from 23 ℃ to 60 ℃ [128]. But no larger temperature range was investigated in their research. However for some chlorobenzenes, their n-octanol/water partition coefficient increased significantly with temperature even at a low temperature range of 5-45 ℃ [129]. For other two complex aromatic compounds, propranolol and atenolol, their n-octanol/water partition coefficients also increased with an increase in temperature[130]. Comparing the extraction results of 5-HMF herein to those from Dumesic et al., we can conclude that P_{HMF} was slightly influenced by temperature as well, and it increased with an increase in temperature.

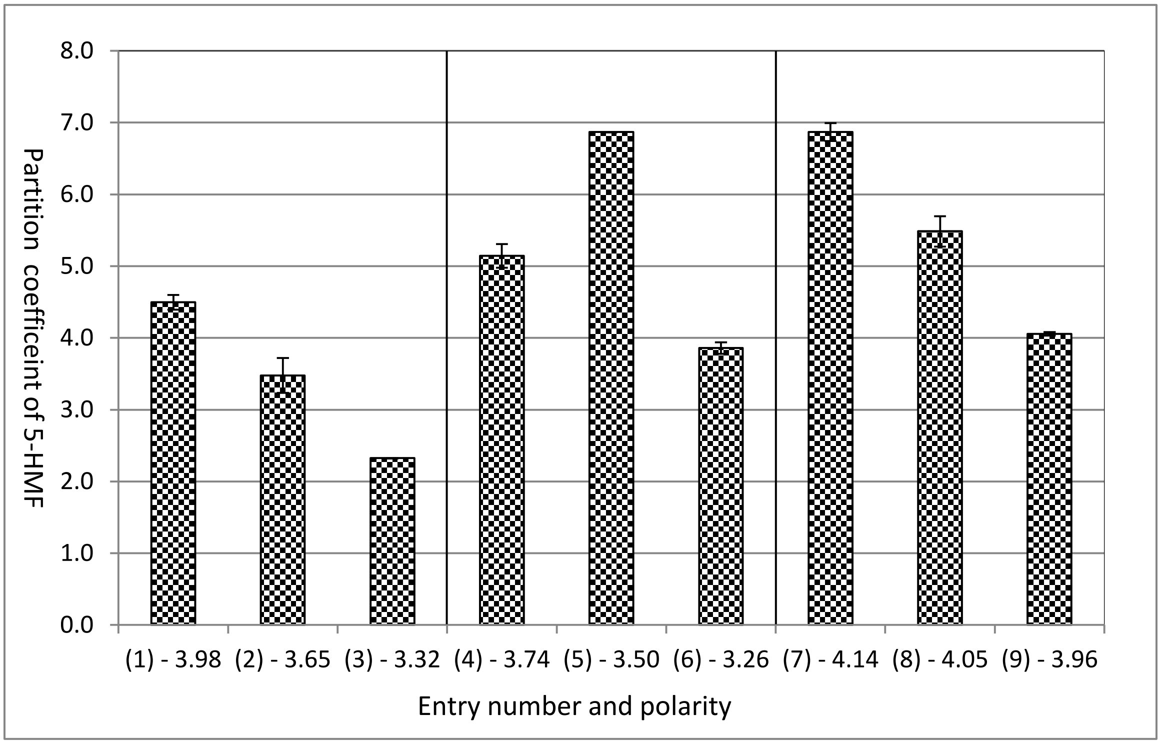

Figure 4-5. P_{HMF} in mixed solvent extraction with 20wt% NaCl at pH 2.4

The extraction performance also depends on the ion concentration in solution. The ions include not only salt ions, but also H_3O^+ and OH^-, which can be generated by dissociation of water or other dissociable compounds, such as organic or inorganic acids. At a high temperature, the ionization constant of water (K_w) increases up to around 10^{-11} [76], which means more water molecules dissociate into H_3O^+ and OH^- ions. In Dumesic's research, the initial pH for reaction was 0.6, which became even lower after reaction and consequently much lower than pH 2.4 in this experiment. The acid in solution also provided more ions, which promoted organic compounds to participate into organic phase to achieve higher partition coefficients. The theory of pH effect on extraction performance will be discussed in detail in Section 4.4.

Besides, the irritation caused by high temperature heating facilitated sufficient mixing of aqueous solution and organic solvent. The extraction was improved because of more effective contact occurred in heating than in manually shaking.

In mixed solvent extraction, the partition coefficients were affected by properties of both solvents. For the extraction of 5-HMF, THF is able to act as the hydrogen bonds accepter, but DCM does not possess the capability to act as hydrogen donor or accepter. Meanwhile, due to the low polarity of DCM, partition coefficients of 5-HMF in Group 1 were not satisfactory. For the extraction of 5-HMF in Group 3, both THF and 2-butanol were able to extract 5-HMF efficiently. Therefore, the mixture showed satisfactory partition coefficient for 5-HMF in mixed solvent as well.

The advantage of my approach is that less NaCl was used to achieve a similarly competitive result. It has been proven that with a higher NaCl concentration in sample solution, more NaCl was brought into organic phase [105]. Although NaCl crystal was also observed in the flask along with the evaporation of organic solvent, less NaCl would appear in the organic phase.

4.2.2 Extraction of levulinic acid and furfural

Partition coefficients of levulinic acid in mixed solvent extraction at pH 2.4 with 20 wt% NaCl are shown in Figure 4-6. Due to property similarities of 5-HMF and levulinic acid, the partition coefficients of levulinic acid exhibited the similar performance with 5-HMF. Mixed solvent extraction with DCM and 2-butanol achieved the greatest partition coefficient of levulinic acid, and mixed solvent extraction with DCM and THF results in the lowest partition coefficient of levulinic acid. These results are consistent with that from single solvent extraction discussed in Section 4.2.1 .

Meanwhile, it was also found that partition coefficients of levulinic acid in all cases were lower than those of 5-HMF. The average recovery rate of 5-HMF in mixed solvent extraction was 81.3% and it was 68.0% for levulinic acid. It indicated that it was easier to extract 5-HMF into the organic phase than levulinic acid with the applied solvent system.

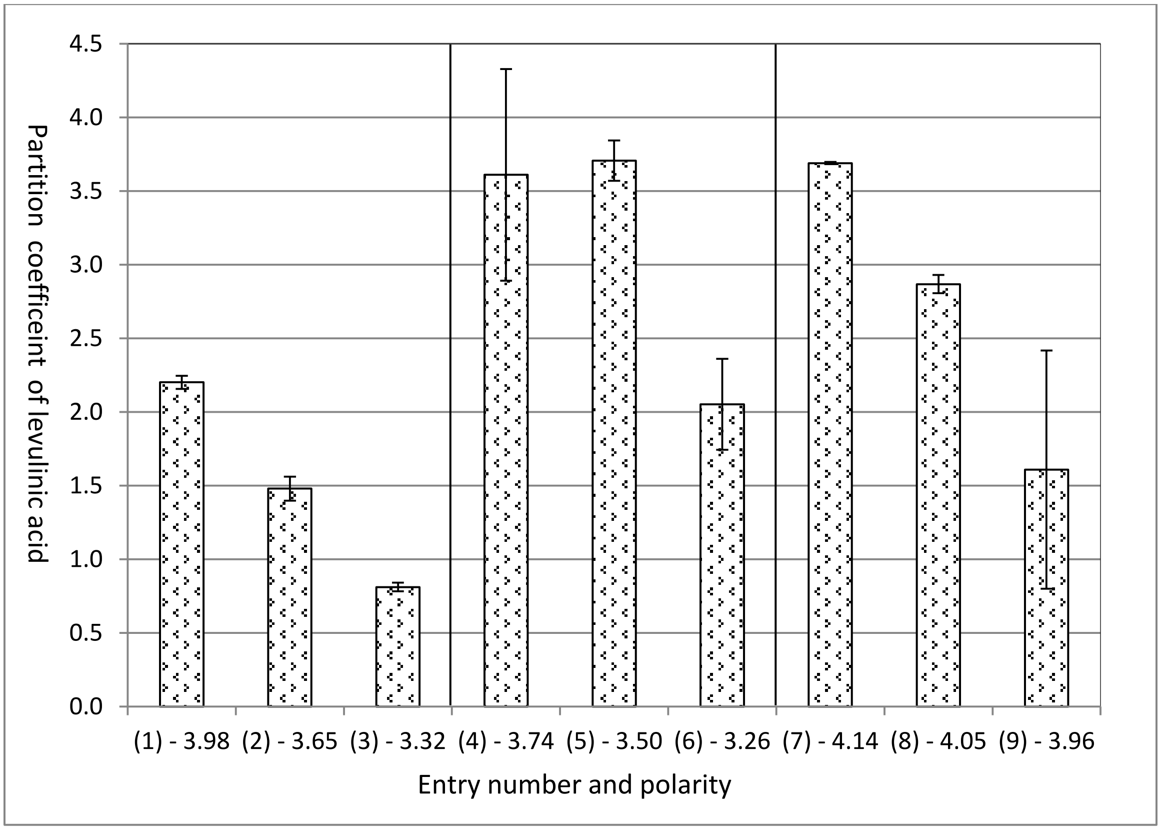

Figure 4-6. P_{LVA} in mixed solvent extraction with 20wt% NaCl at pH 2.4

Partition coefficients of furfural in mixed solvent extraction at pH 2.4 with 20 wt% NaCl are shown in Figure 4-7. Partition coefficients of furfural ranged from 8.13 to 26.83, which are much greater than those of 5-HMF and levulinic acid. Correspondingly, the average recovery rate of furfural from mixed solvent extraction was over 90% (refer to Table 4-1). Compared with the recovery rate of 5-HMF, which was 81% from mixed solvent extraction, this indicated that furfural was much easier to be extracted into organic phase than 5-HMF or levulinic acid owing to the low polarity of furfural. This is also the reason for decreased 5-HMF purity after extraction compared with its initial purity of 77.1%. It is a challenge to 5-HMF separation and purification.

The lowest average value of P_{FF} in mixed solvent extraction was obtained with the mixture of THF and 2-butanol. In the other two groups of mixed solvents containing DCM, the average partition coefficients of furfural were greater. These results revealed that the extraction performance of furfural with mixed solvent was consistent to that of individual solvent. It implies that the extraction of furfural with mixed solvents was affected by the extraction capacity of individual solvents.

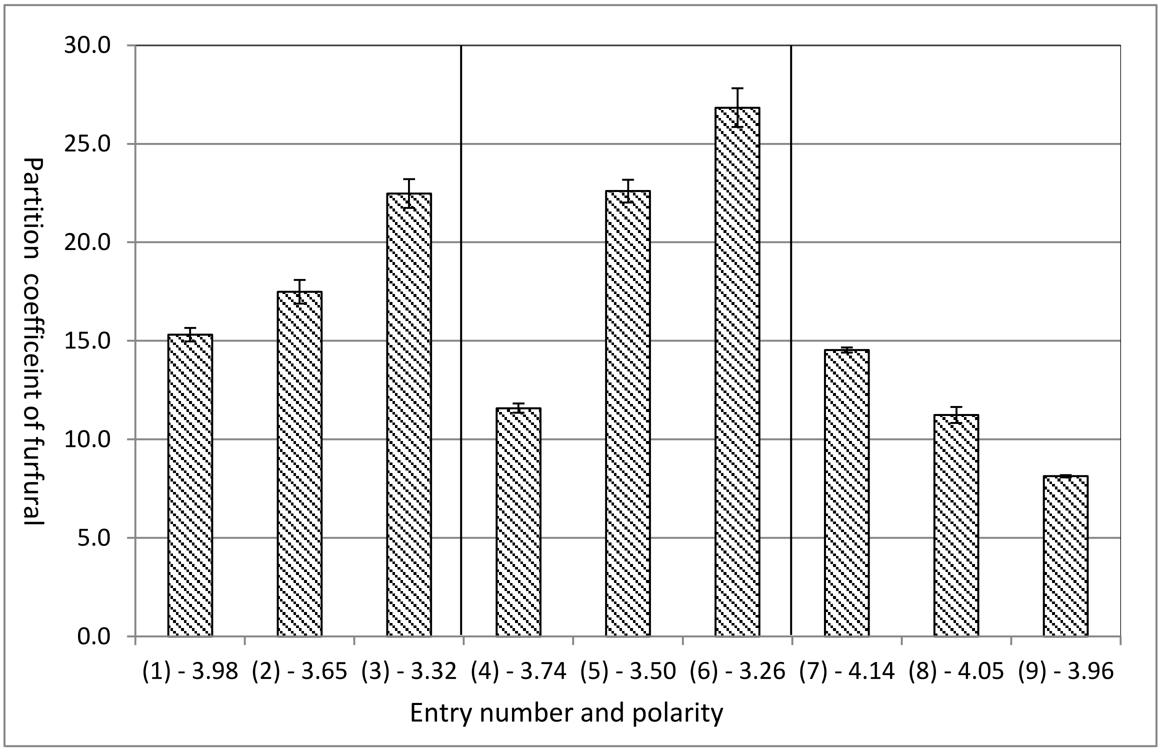

Figure 4-7. P_{FF} in mixed solvent extraction with 20wt% NaCl at pH 2.4

4.2.3 Separation of 5-HMF with levulinic acid and furfural

Separation factors in mixed solvent extraction with 20wt% NaCl at pH 2.4 are shown in Figure 4-8. The separation factors between 5-HMF and levulinic acid were much greater than those between 5-HMF and furfural, and they varied in different groups.

Overall, there was a conflict between 5-HMF extraction efficiency and the separation of 5-HMF from levulinic acid. Separation factors between 5-HMF and levulinic acid were slightly greater for mixed solvent extraction with DCM and THF, but only with very low partition coefficients of 5-HMF. With greater 5-HMF partition coefficients, mixed solvents of DCM with 2-butanol and THF with 2-butanol gave lower average separation factors between 5-HMF and levulinic acid. It was also found that separation factors between 5-HMF and levulinic acid increased with the decrease of the polarity of mixed solvent separately within each group. It can be explained by the phenomena that partition coefficients of levulinic acid increased more significantly than that of 5-HMF with an increase of solvent polarity. However, they were all below 3 in mixed solvent extraction, which means that 5-HMF still was not able to be separated from levulinic acid effectively using the mixed solvent extraction method herein.

Table 4-1 shows the purity of extracted 5-HMF after extraction. Among the three groups, mixed solvent of THF and 2-butanol gave the highest average 5-HMF purity. These results indicate that although the extraction efficiency was improved with mixed solvent extraction method, the separation of 5-HMF with levulinic acid and furfural cannot be achieved with this method. It means that the extraction of 5-HMF was able to be improved with mixed solvent extraction from its aqueous production mixture but without significant improvement in purity.

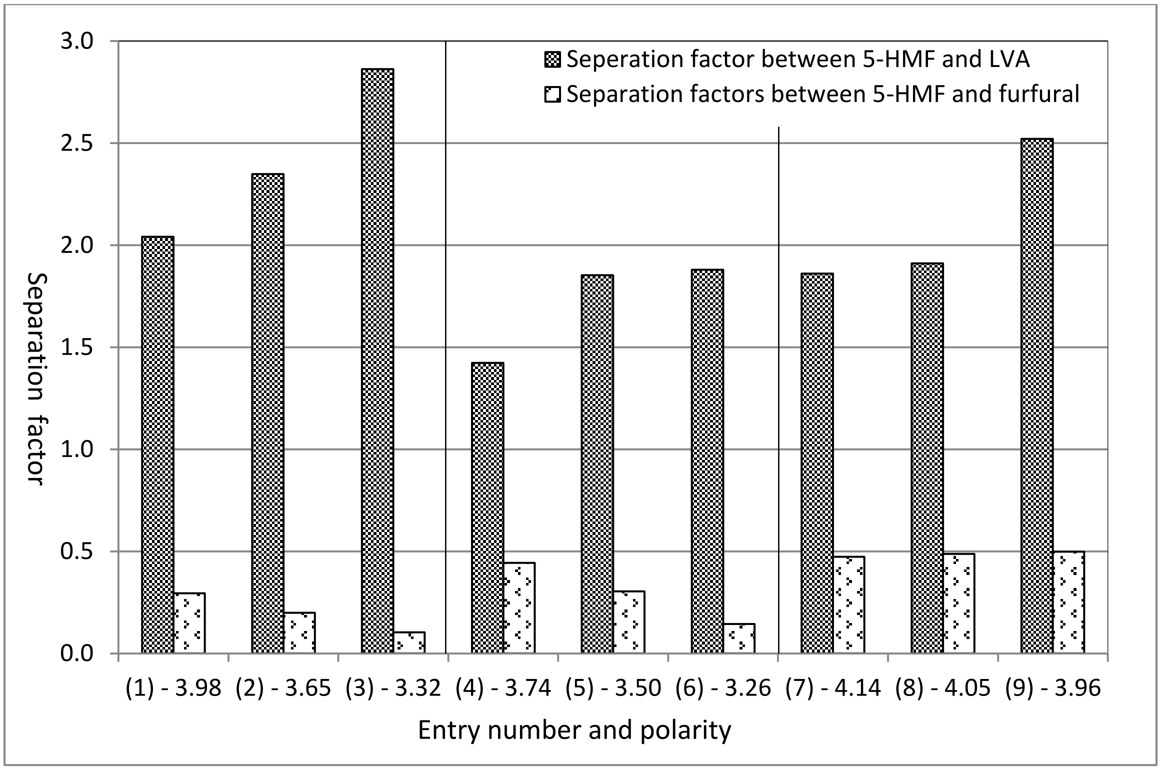

Figure 4-8. Separation factors in mixed solvent extraction with 20wt% NaCl at pH 2.4

4.3 Solvent behavior in mixture

4.3.1 Comparison with theoretical value

In order to study the performance of mixed solvents for 5-HMF extraction, measured partition coefficients of 5-HMF in experiments were compared with calculated values with Eq.(16). The results are shown in Table 4-2. Compared with single solvent extraction, performance of mixed solvent was affected by solvent mixing. The results also indicated that mixing of different solvents exhibited distinct influences on 5-HMF extraction. In DCM-THF and 2-butanol-THF mixed solvent extraction, partition coefficient of 5-HMF was not significantly enhanced by the mixing of two solvents. Actually, for some entries, mixed solution resulted in the decrease of partition coefficient of 5-HMF. In DCM-2-butanol mixed solvent extraction, partition coefficient of 5-HMF was greatly increased, and Entry 5 showed the most significant increase, which was as high as 171.9%.

Table 4-2. Comparison between theoretical values of P_{HMF} and experiment data of P_{HMF} with 20wt% NaCl at pH2.4

Group No.	Solvent	Entry No.	Calculated P_{HMF}	Experimental data of P_{HMF}	Increasing rate*
1	DCM-THF	1	4.98	4.50	-9.7%
		2	3.52	3.48	-1.2%
		3	2.06	2.32	12.9%
2	DCM-2-butanol	4	3.39	5.14	51.7%
		5	2.53	6.87	171.9%
		6	1.66	3.86	132.3%
3	2-butanol-THF	7	5.55	6.87	23.6%
		8	4.96	5.48	10.6%
		9	4.36	4.06	-7.0%

* Increasing rate is calculated via dividing experimental data of P_{HMF} by calculated P_{HMF}, which indicates the differences between measured and predicted data.

For mixing solvents, the advantage is that different solvents have diverse properties, which may be involved in different interactions between the solute and the solvent molecules. The improved extraction performance of mixed solvents may be attributed to the protic and aprotic properties of the solvents. Depending on whether they have capability to exchange protons (H^+), an organic solvent can be classified to be protic and aprotic [131]. Protic solvents act as proton donors in hydrogen bond, and aprotic solvents cannot donate hydrogen. 2-butanol is a protic solvent, since it has a hydroxyl group in its structure, which can participate in proton exchange. On the contrary, DCM and THF are aprotic solvents without H^+ that is exchangeable under certain condition. This feature determines their capacity to form hydrogen bones with water or solutes. The formation of hydrogen bond affected not only the extraction performance, but also affected the retention of solvent in aqueous phase.

In Group 1, both of DCM and THF are aprotic solvents. Although hydrogen bonds can be formed between the hydroxymethyl group in 5-HMF and the oxygen atom in THF, the extraction performance was not significantly improved by solvent mixing. For mixed solvents of DCM with 2-butanol and THF with 2-butanol, each group was composed of one protic solvent and one aprotic solvent. P_{HMF} was significantly increased in Group 2, but only slightly improved in Group 3. The difference in capability of hydrogen donating may lead to different interactions between the solvents and the solute, which was responsible for the improved extraction performance.

4.3.2 Volume ratio effect on extraction

The relationships between organic solvent volume fraction and solute partition coefficients in each solvent group are shown in Figure 4-9, Figure 4-10 and Figure 4-11. Partition coefficients of 5-HMF and partition coefficients of levulinic acid are shown at the primary y-axis, and partition coefficients of furfural are shown in the secondary y-axis.

The partition coefficients of all three solutes displayed a linear correlation with solvent volume fraction in DCM-THF and 2-butanol-THF mixed solvents extraction. The exception was the group of DCM-2-butanol mixed solvent, in which the linear correlation existed only in furfural extraction (shown in Figure 4-10). This phenomenon also appeared in the extraction with 10wt% NaCl at pH 2.4 and the extraction with 20wt% NaCl at pH 2.0.

This linear correlation indicated that the organic solvents in mixed solvent extraction functioned independently to solvent volume faction for the condition in this thesis work. It can be proven by the following.

Since $x_B = 1 - x_A$, Eq. (19) $P_0 = \frac{C_{org}}{C_{aq}} = x_A P_A + x_B P_B$ can be written as

$$P_0 = x_A P_A + (1 - x_A) P_B = (P_A - P_B) x_A + P_B \qquad \text{`} \qquad (21)$$

If the partition behavior of solutes in different solvents were independent on its volume fraction, it can be assumed that P_A and P_B are independent on the volume fraction x_A and x_B, which means that P_A and P_B are all constants.

To test this assumption, the linear correlation equations for furfural and levulinic acid in charts were substituted to Eq. (21). The linear correlation of partition coefficient of 5-HMF with volume fraction disappeared in Group 2, so it was not included in this test. The following results were determined from each group.

For extraction of levulinic acid,

a) From mixed solvent of DCM with THF

$P_{THF} = 2.7$ $P_{DCM} = 0.3$

b) From mixed solvent of DCM with 2-butanol

$P_{2-B} = 4.4$ $P_{DCM} = 1.8$

c) From mixed solvent of THF with 2-butanol

$P_{THF} = 4.5$ $P_{2-B} = 1.0$

For extraction of furfural,

a) From mixed solvent of DCM with THF

$P_{THF} = 12.5$ $P_{DCM} = 24.4$

b) From mixed solvent of DCM with 2-butanol

$P_{2-B} = 7.6$ $P_{DCM} = 33.0$

c) From mixed solvent of THF with 2-butanol

$P_{THF} = 16.6$ $P_{2-B} = 6.0$

The results above show that partition coefficients for the same solvent varied from one group to another. It can be concluded that P_B and P_A are not constant in mixed solvent, which means the extraction capacities of individual organic solvent in mixed solvents was affected by solvent mixing. Therefore, we can assume that P_A and $P_B$are a function of volume fraction of solvent A (x_A) and B (x_B) respectively $P_A = f(x_A)$ and $P_B = g(x_B)$.

Since $x_B = 1 - x_A$, then $P_B = g(x_B) = g(1 - x_A)$. Then let $g(1 - x_A) = h(x_A)$, thus $P_B = h(x_A)$.

Classify the items in $f(x_A)$ and $h(x_A)$ into constant terms and non-constant terms. The constant parts in $f(x_A)$ and $h(x_A)$ are denoted as m and n separately, and the non-constant terms are denoted as $u(x_A)$ and $v(x_A)$. Then P_A and P_B can be written as $P_A = f(x_A) = u(x_A) + m$ and $P_B = h(x_A) = v(x_A)$ +n.

Substituting it into Eq. (21), and rearranging

$$P_0 = (P_A - P_B)x_A + P_B = [u(x_A) + m - v(x_A) - n]x_A + [v(x_A) + n]$$

$$= \underbrace{\{v(x_A) + [u(x_A) - v(x_A)]x_A\}}_{\text{A}} + \underbrace{\{[m - n]x_A + n\}}_{\text{B}} \qquad (22)$$

After rearrangement, it can be concluded that the items in the second bracket is linear. Only if the terms in the first bracket $\{v(x_A) + [u(x_A) - v(x_A)]x_A\}$, is linear, or it is constant with $m - n \neq 0$ and $n \neq 0$, the whole equation can be linear.

However, according to the assumption that $u(x_A)$ and $v(x_A)$ are non-constant terms, the terms in the first bracket (marked as A part in Eq.(22)) cannot be a constant, and it can only be a function of x_A or zero. Only if $[u(x_A) - v(x_A)]x_A = 0$, which means that $u(x_A) = v(x_A)$, and $v(x_A)$ is linear, then $\{v(x_A) + [u(x_A) - v(x_A)]x_A\}$ will be linear with x_A. Therefore, it was concluded that the prerequisite of the linear correlation displayed in charts is that P_B and P_A are linear functions of the volume fraction of the solvent.

The special extraction performance of mixed solvent Group 2 was possibly related to the phenomena of solvation. When a solute dissolved in a solvent, the solute molecules are surrounded by the solvent molecules to form a solvent shell on the outer space of solute molecules. According to the components of solvent shell in mixed solvent, solvation can be classified into two categories. One is non-selective solvation, and the other is selective solvation. In non-selective solvation, the molecule numbers in solvation shell equals to the molecule ratio of individual solvents in mixed solvent. In selective solvation, the molecule numbers in solvation shell do not equal to the molecule ratio in bulk solvent [132]. For organic compound molecule, there may be similar phenomena occurring between the solvent and solute molecules due to the property difference between different parts in their structures.

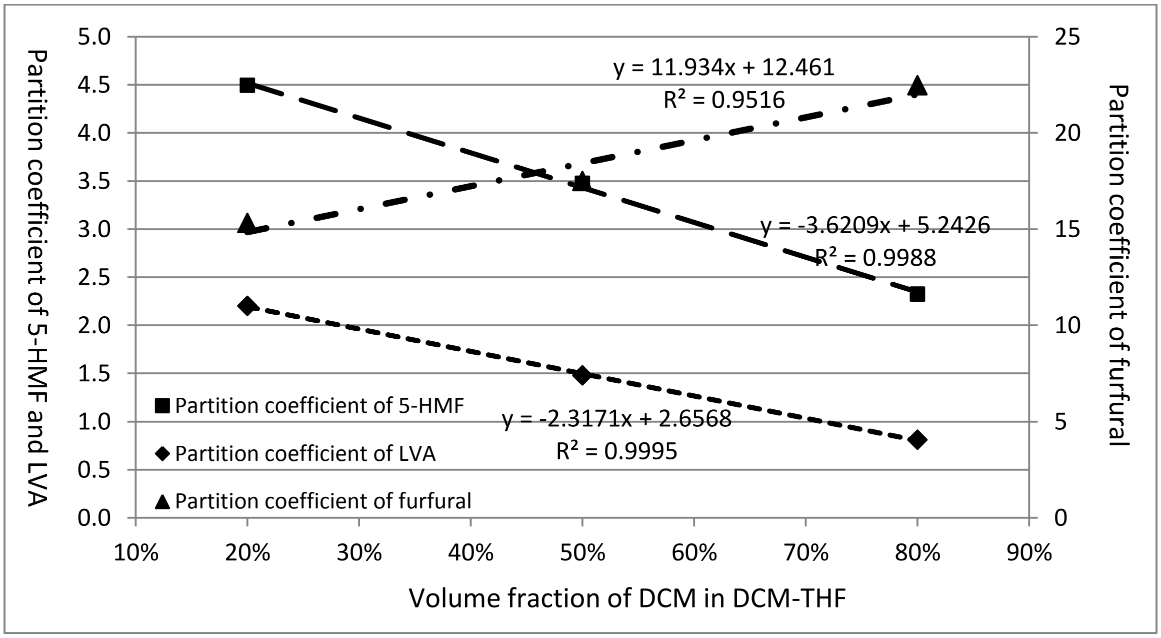

Figure 4-9. Correlationsihp between partition coefficients of solutes and solvent volume fraction in Group 1 with 20wt% NaCl at pH 2.4

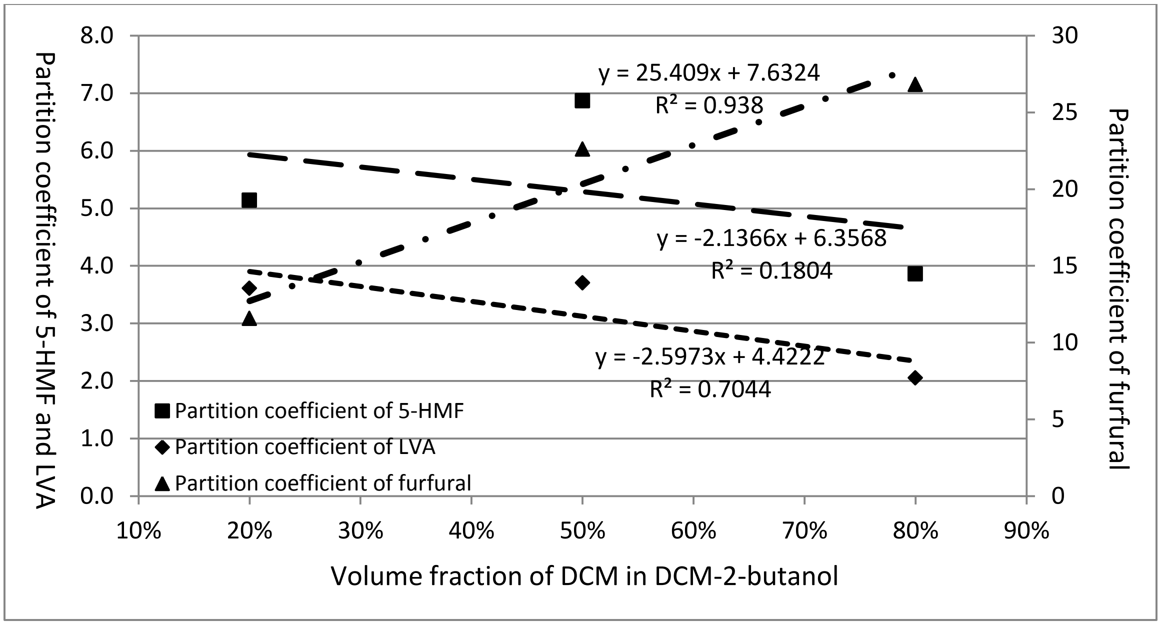

Figure 4-10. Correlationsihp between partition coefficients of solutes and solvent volume fraction in Group 2 with 20wt% NaCl at pH 2.4

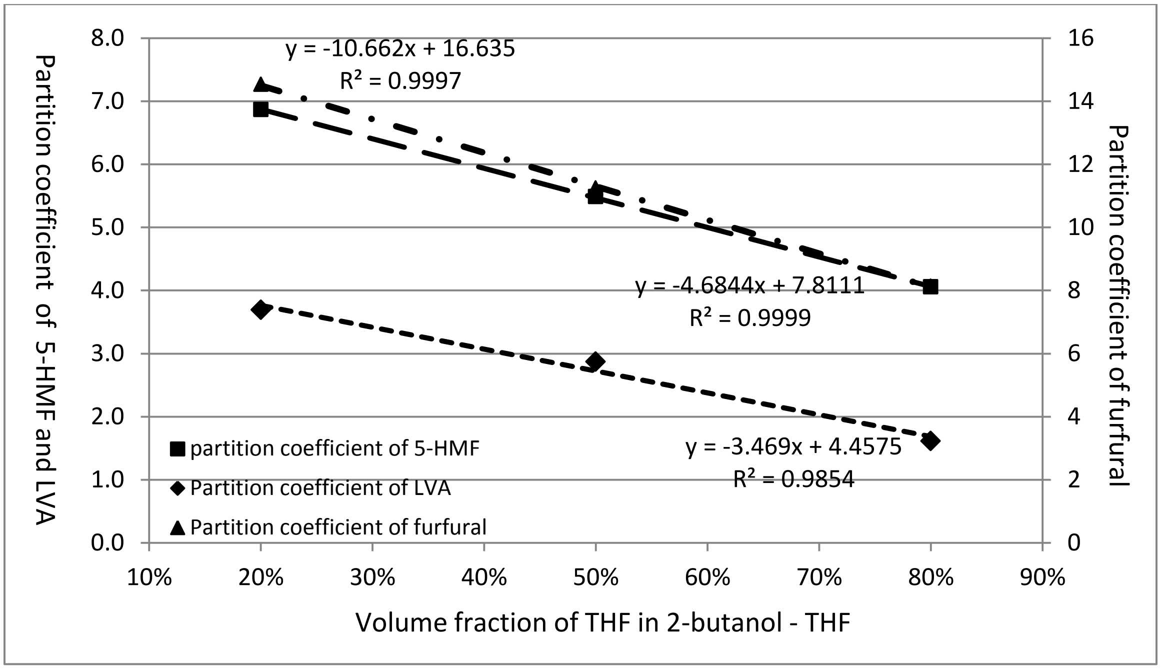

Figure 4-11. Correlationsihp between partition coefficients of solutes and solvent volume fraction in Group 3 with 20wt% NaCl at pH 2.4

Mixed solvent in Group 2 is composed of DCM and 2-butanol. DCM is a non-polar small molecule, which prefers to interact with non-polar structure in molecules, such as the furan ring in 5-HMF. 2-butanol has high polarity with larger molecular size, and the hydroxyl group in its structure can act as hydrogen donor to form hydrogen bonds with 5-HMF. Adjust the molar ratio of these two solvents can affect their extraction performance. The organic solvents were mixed by volume ratio, and according to their molar weights and densities, the theoretical molar ratio and fractions can be determined. The calculation results are shown in Table 4-3. From the result and data in Table 4-3, we can find the suitable molar ratio for 5-HMF extraction in certain mixed solvent. In Entry 5, the molar fraction was about 11/8. Assuming that there is no selective solvation, the molar ratio in solvent shell was the same as that in bulk solvent. It means that, compared with 2-butanol, about 1.5 times DCM molecules exist in solvent shell. If selective solvation is taken into consideration, the results would be too sophisticated to be analyzed. With present results, the specific interactions between solutes and solvent molecules cannot be identified and explained accurately. It is concluded from our results that the behavior of mixed solvent in extraction was different from single solvent extraction and it was influenced by solvent mixing.

Table 4-3. Theoretical molar ratio and fractions of mixed organic solvent in extraction with NaCl

Group No.	Solvent	Entry No.	Solvent volume ratio	Theoretical molar ratio	Molar fraction
1	DCM-THF	1	1 : 4	0.30	2/7
		2	1 : 1	1.19	6/5
		3	4 : 1	4.76	19/4
2	DCM - 2-butanol	4	1 : 4	0.34	1/3
		5	1 : 1	1.38	11/8
		6	4 : 1	5.51	11/2
3	2-butanol -THF	7	1 : 4	0.22	2/9
		8	1 : 1	0.86	6/7
		9	4 : 1	3.45	31/9

4.4 Effect of pH value

The pH effect on partition coefficient and separation factor with 20wt % NaCl at pH 2.0 and pH 2.4 are shown in Table 4-4. According to the results in Table 4-4, when pH decreased from pH 2.4 to pH2.0, the average P_{HMF} for each group did not change much for mixed solvent extraction of DCM with THF and

DCM with 2-butanol, but it decreased when a mixed solvent of THF and 2-butanol was employed. Levulinic acid extraction was improved by lower pH in mixed solvent extraction with DCM and THF and THF and 2-butanol. In mixed solvent extraction with DCM and 2-butanol, P_{LVA} decreased with the lower pH. On average, furfural extraction was almost independent of pH value, since the changing rates were only 2% - 3%. Overall, pH had a stronger influence on levulinic acid extraction than 5-HMF and furfural.

With a dissociation constant pKa of 4.59, the existing form of levulinic acid in aqueous solution is affected by pH due to the dissociation of carboxyl group in its structure [133]. The existing excessive proton in solution of lower pH value could hinder the dissociation of carboxyl group in levulinic acid in acidic solution. Levulinic acid exists more as molecule at lower pH value, which tends to participate into organic phase much easier than disassociated ions with less electric charge. Therefore, it is more favorable to be extracted by an organic solvent in acidic solution. 5-HMF and furfural do not have functional groups which can undergo strong dissociation in their structures, so their partition between aqueous and organic phase did not depend on the pH. The dissociation of 5-HMF (pKa =12.82) was negligible under the pH range in this experiment and 5-HMF mainly existed in the form of molecules [3].

Table 4-4. pH effect on partition coefficient in extraction with 20wt% NaCl (pH 2.0/pH 2.4)

Group No.	Solvent	Entry No.	P_{HMF} ratio	P_{LVA} ratio	P_{FF} ratio	S_1 ratio*	S_2 ratio**
1	DCM-THF	1	0.97	1.22	1.02	0.79	0.95
		2	1.03	1.20	1.07	0.86	0.96
		3	1.05	1.36	0.98	0.77	1.07
		Average	1.02	1.26	1.03	0.81	0.99
2	DCM-2-butanol	4	1.00	0.53	1.07	1.89	0.94
		5	0.80	0.44	0.83	1.82	0.96
		6	1.04	0.85	1.03	1.23	1.01
		Average	0.95	0.60	0.97	1.65	0.97
3	2-butanol-THF	7	0.71	1.31	0.92	0.55	0.77
		8	0.97	1.23	1.02	0.78	0.95
		9	0.89	1.49	0.98	0.60	0.91
		Average	0.86	1.34	0.98	0.64	0.87

* S_1 ratio refers to the ratio of S_1 in extraction at pH 2.0 to S_1 in extraction at pH 2.4 with 20% NaCl.

** S_2 ratio refers to the ratio of S_2 in extraction at pH 2.0 to S_2 in extraction at pH 2.4 with 20% NaCl.

These results can be verified by calculating the concentration of dissociated ions in solution with Henderson–Hasselbalch equation [134].

$$pK_a - pH = -\log_{10}\frac{[A^-]}{[HA]} \tag{23}$$

HA is a weak acid, which is able to release hydrogen ions via dissociation. $[A^-]$ stands for the concentration of dissociated ions of HA, $[HA]$ is the concentration of molecule form of HA. The initial total molecule concentration of HA is denoted as $[HA]_0$.

$$[HA] = [HA]_0 - [A^-] \tag{24}$$

$$-\log_{10}\frac{[A^-]}{[HA]} = \log_{10}\frac{[HA]}{[A^-]} = \log_{10}\frac{[HA]_0-[A^-]}{[A^-]} = \log_{10}(\frac{[HA]_0}{[A^-]} - 1) \tag{25}$$

$$pK_a - pH = \log_{10}(\frac{[HA]_0}{[A^-]} - 1) \tag{26}$$

For 5-HMF, $K_a = 12.82$, when pH = 2.0 and 2.4 respectively,

$$\log_{10}\left(\frac{[HA]_0}{[A^-]_{2.0}} - 1\right) = 12.82 - 2.0 = 10.82 \tag{27}$$

$$\log_{10}\left(\frac{[HA]_0}{[A^-]_{2.4}} - 1\right) = 12.82 - 2.4 = 10.42 \tag{28}$$

$$\frac{[HA]_0}{[A^-]_{2.0}} - 1 = 6.607 \times 10^{10} \tag{29}$$

$$\frac{[HA]_0}{[A^-]_{2.4}} - 1 = 2.630 \times 10^{10} \tag{30}$$

In Eq.(29) and (30), compared to the number with magnitude of 10^{10} on the right side, -1 on the left side is negligible. Then we got

$$\frac{[HA]_0}{[A^-]_{2.0}} \approx 6.607 \times 10^{10} \tag{31}$$

$$\frac{[HA]_0}{[A^-]_{2.4}} \approx 2.630 \times 10^{10} \tag{32}$$

Form the simplified results above, one can get the conclusion that although

$$\frac{[A^-]_{2.4}}{[A^-]_{2.0}} \approx 2.5 \tag{33}$$

Compared with initial concentration of $[HA]_0$, an variation in $[A^-]$ is still too small to show significant influence on extraction performance.

For levulinic acid, $pK_a = 4.59$

$$\log_{10}\left(\frac{[HA]_0}{[A^-]_{2.0}} - 1\right) = 4.59 - 2.0 = 2.59 \tag{34}$$

$$\log_{10}\left(\frac{[HA]_0}{[A^-]_{2.4}} - 1\right) = 4.59 - 2.4 = 2.19 \tag{35}$$

After calculation, one gets

$$\frac{[HA]_0}{[\,A^-]_{2.0}} = 390.0 \qquad (36)$$

$$\frac{[HA]_0}{[\,A^-]_{2.4}} = 155.9 \qquad (37)$$

For levulinic acid, $\frac{[\,A^-]_{2.4}}{[\,A^-]_{2.0}}$ has the same magnitude of 2.5 as the results from 5-HMF. However, the absolute concentration difference between $[\,A^-]_{2.0}$ and $[\,A^-]_{2.4}$ are much greater than that of 5-HMF. This calculation is one supporting verification of the experimental result that pH has a great influence on levulinic acid extraction.

In Table 4-4, separation factors between 5-HMF and levulinic acid S_1 was affected by pH change greater than separation factors between 5-HMF and furfural S_2 on average. This is because, as discussed above, P_{LVA} involved in this separation factor was affected greater by pH change. When pH decreased from 2.4 to 2.0, all average separation factors decreased except for S_1 using mixed solvent extraction with DCM and 2-butanol. It implies that adjusting pH from 2.4 to 2.0 is not an effective way to improve 5-HMF separation with levulinic acid and furfural.

4.5 Effect of NaCl concentration

4.5.1 Effect of NaCl concentration on extraction

Table 4-5 summarizes the effect of NaCl concentration on the extraction performance, which shows that partition coefficients of all three solutes increased with NaCl concentration. This is consistent with ‘salting-out effect’ theory, and similar phenomenon has been reported for 5-HMF extraction with 1-butanol and 2-butanol carried out by Dumesic et al. [105].

Table 4-5 shows that different solutes had different sensitivities to NaCl concentration, and the same solute had different sensitivities in extraction with different solvents. This was attributed most likely to the complex interactions among water, solute, solvent molecules and salt. These interactions include hydrogen bonds, solvation of solvent and solute molecules, and solvation of salt ions. The extraction performances were influenced by the properties of both solvents and solutes. As mentioned above, ‘salting-out effect’ is attributed to the solvation of salt ions, which makes water molecule unavailable to solute molecules [135]. Among the three solutes used herein, levulinic acid has the strongest interaction with water. Hydrogen bonds can be formed between its carboxyl group and water molecules, and its dissociated ions can be solvated by water. Both of these two types of interactions can be weakened by the presence of NaCl. Although the hydroxyl group in 5-HMF also is able to be dissociated, it is much more difficult than that of levulinic acid. Therefore, the partition coefficients of levulinic acid were affected by NaCl concentration most significantly.

Table 4-5. NaCl concentration effect on partition coefficients at pH 2.4 (20wt% NaCl/10wt% NaCl)

Group No.	Solvent	Entry No.	P_{HMF} ratio	P_{LVA} ratio	P_{FF} ratio	S_1 ratio*	S_2 ratio**
1	DCM-THF	1	1.50	1.66	1.43	0.90	1.05
		2	1.50	1.35	1.45	1.11	1.03
		3	1.29	1.13	1.25	1.14	1.03
		Average	1.43	1.38	1.38	1.05	1.04
2	DCM-2-butanol	4	1.49	2.00	1.42	0.75	1.05
		5	1.53	1.57	1.42	0.97	1.07
		6	1.53	1.99	1.31	0.77	1.17
		Average	1.51	1.85	1.38	0.83	1.10
3	2-butanol-THF	7	1.81	1.68	1.84	1.08	0.99
		8	1.58	1.4	1.58	1.13	1.00
		9	1.47	0.93	1.44	1.58	1.02
		Average	1.62	1.34	1.62	1.26	1.00

* S_1 ratio refers to the ratio of S_1 in extraction with 20% NaCl to S_1 in extraction with 10%NaCl at pH 2.4.

** S_2 ratio refers to the ratio of S_2 in extraction with 20% NaCl to S_2 in extraction with 10%NaCl at pH 2.4.

For the mixed solvent extraction of DCM with THF mixed solvent, there were only aprotic organic solvents, in which different solutes exhibited similar sensitivity to NaCl concentration change. For the mixed solvent extraction of DCM and 2-butanol, the increase of NaCl concentration resulted in higher extraction selectivity for levulinic acid. Considering the ‘like-dissolves-like’ theory [131], it can be deduced from this result that in this group 2-butanol had dominant effect on partition coefficient with the increase of NaCl concentration. However, in mixed solvent extraction with THF and 2-butanol, 5-HMF and furfural gave higher sensitivity than levulinic acid. This means that THF exerted the dominant effect on the increase of partition coefficients with NaCl concentration here. This is because the solubility of THF in aqueous solution depended on NaCl concentration. At a higher concentration of NaCl, less THF was able to exist in aqueous phase and more THF was forced to move into the organic phase. Since the existence of THF in organic phase is favorable for the extraction of solutes with furan ring in its structure, 5-HMF and furfural were more favorable to be extracted than levulinic acid with higher NaCl concentration. It also can be verified by the results in mixed solvent extraction using DCM and THF, in which 5-HMF and furfural exhibited slightly greater sensitivity than levulinic acid in Entry 2 and 3.

4.5.2 Effect of NaCl concentration on separation

Table 4-5 also showed that for mixed solvent extraction with DCM and THF, S_2 remained almost the same, while the S_2 varied from -10% to 14%. In mixed solvent extraction with DCM and 2-butanol, S_2 increased from 5% to 17% and S_1 decreased from 3% 25%. In mixed solvent extraction with THF and 2-butanol, S_1 increased from 8% to 58%, whereas S_2 almost remained the same. It can be summarized that high NaCl concentration always benefited 5-HMF extraction, but it was not the case for the separation of 5-HMF from other compounds. The separation factor between 5-HMF and levulinic acid increased most significantly for mixed solvent extraction with THF and 2-butanol.

An increase in NaCl concentration improved the separation of 5-HMF and levulinic acid in mixed solvent extraction of DCM with THF and 2-butanol with THF, but exhibited negative effect in mixed solvent extraction of DCM with 2-butanol. Meanwhile, NaCl concentration only displayed slight influence on separation of 5-HMF and furfural.

4.6 Organic solvent recovery

Extraction systems with different solvents mixture had different solvent recovery rates, as shown in Table 4-6. The recovery rate of organic solvent did not have a simple proportional relationship with their individual solubility in water. Although mixed solvent of DCM and 2-butanol had the outstanding performance in the extraction and separation of 5-HMF, its solvent recovery is the lowest. Only around 90% of the solvent could be recovered with mixed solvent extraction with DCM and THF, as well as with DCM and 2-butanol.

There are two factors affecting the solvent recovery rate. One is the evaporation of organic solvent. Solvent with higher vapor pressure tended to lose larger volume via evaporation. Therefore, the mixed solvent with DCM in it showed a lower solvent recovery rate on average. The other factor is the mutual solubility of organic solvent with water. In many organic solvent-salt–water systems, although the ‘salting-out effect’ enhances the phase separation of aqueous solution and organic solvent, there is still a certain amount of organic solvent dissolved in the aqueous phase [136]. The low recovery rate of organic solvent in mixed solvent extraction with DCM and 2-butanol might be caused by the strong interaction between 2-butanol with water through hydrogen bonds.

It has also been proven that DCM, 2-butanol and THF are all able to form hydrogen bonds with water molecules [125, 137, 138]. With a higher concentration of NaCl, water molecules tended to be occupied by NaCl solvation instead of solvation of solutes. Therefore, more organic solvent molecules were likely released from hydrogen bond connection with water, and it was supposed to give a higher solvent recovery rate with a higher concentration of NaCl. However, only mixed solvent extraction with DCM and THF achieved higher solvent recovery rate with 20wt% NaCl than that with 10wt% NaCl. Using mixed solvent of DCM with 2-butanol and THF with 2-butanol, the solvent recovery rates decreased, both for 20% NaCl. It was reported that in water-2-butanol-NaCl system, 2-butanol can form $Na^+(2\text{-}BuOH)_2Cl^-$ complex with an equilibrium constant of 0.11 [139], which will enhance the retention of 2-butanol in the aqueous solution. The phenomenon that extraction with higher a NaCl concentration gave a lower solvent recovery rate might imply the existence of $Na^+(2\text{-}BuOH)_2Cl^-$ complex in the extraction system. With 20wt% NaCl, more $Na^+(2\text{-}BuOH)_2Cl^-$ complex could be formed, which results in more 2-butanol retained in the aqueous phase and the lower organic solvent recovery rate in extraction with 20wt% NaCl than that in extraction with 10wt% NaCl.

Table 4-6. Solvent recovery rate with 20wt% NaCl at pH 2.4

Group No.	Solvent	Entry No.	with 20wt% at pH 2.4/ %	with 10wt% at pH 2.4/ %
1	DCM-THF	1	92	86
		2	90	94
		3	96	88
		Average	93	89
2	DCM-2-butanol	4	90	92
		5	82	84
		6	92	92
		Average	88	89
3	2-butanol-THF	7	96	98
		8	96	96
		9	92	98
		Average	95	97

Chapter 5

Conclusions and recommendations for future work

It was found that the extraction of 5-HMf using organic solvents was influenced by several factors, including solvent polarity, solvent molecule structure, and solvent hydrogen donating feature. For single solvents, high polarity was favorable for 5-HMF extraction. However, high polarity also created the conflict between extraction and separation of 5-HMF and levulinic acid. Compared with single solvent extraction, mixed solvent extraction gave better performance for 5-HMF extraction than that with single solvents. In mixed solvent extraction, the partition coefficients of solutes did not always show the simple correlation with solvent polarity. The extraction capacities of mixed solvents did not behave independently in mixed solvents, although the partition coefficients of solutes displayed linear correlation with solvent mixing fraction in some mixed solvent groups. Their extraction capacities were affected by mixing, and exhibited a complicated relationship with solvent mixing ratio.

Among three groups, higher partition coefficient of 5-HMF, better separation of 5-HMF with furfural, higher 5-HMF purity in product and a higher solvent recovery rate were achieved by mixed solvent extraction with THF and 2-butanol. In this group, entry 7 (v/v for 2-butanol:THF = 1:4) is the most favorable solvent combination for 5-HMF extraction. It can be summarized that considering extraction and separation performance together, extraction with 20wt% NaCl at pH 2.4 is the favorable condition for 5-HMF extraction.

Increasing NaCl concentration significantly increased the partition coefficients of all three solutes due to 'salting-out' effect. However, the separation factors between 5-HMF with levulinic acid and furfural were not improved significantly. Adjusting pH level in a small range had a strong influence on the partition coefficients of levulinic acid, but not for 5-HMF or furfural. Therefore, the separation factors between 5-HMF and levulinic acid were influenced more significantly than the separation factors between 5-HMF and furfural. After extraction, around 90% of applied organic solvent could be recovered, which makes this process economically feasible.

Recommendations for future work include investigating the special behavior of mixed solvent of DCM and 2-butanol in 5-HMF extraction, applying mixed solvent in real hydrothermal conversion product and two-phasic 5-HMF synthesis system to test their extraction capacity for the simultaneous extraction of 5-HMF during reaction.

Appendix

Table A-1. P_{HMF}, P_{LVA}, P_{FF}, separation factors and purification of 5-HMF after extraction with 20wt% NaCl at pH 2.4

Entry No.	Organic solvent	P_{HMF}	Stedv. of P_{HMF}	P_{LVA}	Stedv. of P_{LVA}	P_{FF}	Stedv. of P_{FF}	R_{HMF} (%)	R_{LVA} (%)	R_{FF} (%)	Purity of 5-HMF (%)	S_1	S_2
1	DCM+THF/1:4	4.50	10.1%	2.20	4.4%	15.31	33.6%	81.8	68.8	93.9	75.7	2.04	0.29
2	DCM+THF /1:1	3.48	24.4%	1.48	8.1%	17.50	59.7%	77.7	59.7	94.6	75.3	2.35	0.20
3	DCM+THF/4:1	2.32	0.2%	0.81	2.9%	22.47	73.0%	69.9	44.8	95.7	74.2	2.86	0.10
4	DCM+2-B/1:4	5.14	16.5%	3.61	71.9%	11.58	23.5%	83.7	78.3	92.1	75.7	1.42	0.44
5	DCM+2-B/1:1	6.87	0.1%	3.71	13.7%	22.60	57.6%	87.3	78.8	95.8	75.9	1.85	0.30
6	DCM+2-B/4:1	3.86	8.0%	2.05	30.8%	26.83	98.1%	79.4	67.2	96.4	74.9	1.88	0.14
7	2-B +THF/1:4	6.87	12.5%	3.69	0.8%	14.53	13.0%	87.3	78.7	93.6	76.3	1.86	0.47
8	2-B +THF /1:1	5.48	21.3%	2.87	6.2%	11.24	41.0%	84.6	74.2	91.8	76.2	1.91	0.49
9	2-B +THF /4:1	4.06	2.4%	1.61	80.8%	8.13	5.4%	80.2	61.7	89.1	76.6	2.52	0.50
10	THF	5.95	2.8%	3.956	6.6%	14.12	45.4%	85.6	79.8	93.4	75.9	1.50	0.42
11	2-Butanol	3.965	0.9%	2.90	2.4%	4.98	10.0%	79.9	74.4	83.3	76.4	1.37	0.80
12	DCM	1.08	2.4%	- 0.22	0.3%	31.22	28.9%	52.0	-	96.9	-	-	0.03

Table A-2. P_{HMF}, P_{LVA}, P_{FF}, separation factors and purification of 5-HMF after extraction with 10wt% NaCl at pH 2.4

Entry No.	Organic solvent	P_{HMF}	Stedv. of P_{HMF}	P_{LVA}	Stedv. of P_{LVA}	P_{FF}	Stedv. of P_{FF}	R_{HMF} (%)	R_{LVA} (%)	R_{FF} (%)	Purity of 5-HMF (%)	S_1	S_2
1	DCM+THF/1:4	3.00	6.1%	1.33	19.1%	10.68	18.8%	75.0	57.0	91.4	74.3	2.26	0.28
2	DCM+THF /1:1	2.32	6.7%	1.09	14.3%	12.09	16.9%	69.9	52.3	92.4	73.5	2.12	0.19
3	DCM+THF/4:1	1.80	3.3%	0.72	1.1%	17.93	2.3%	64.3	41.8	94.7	73.1	2.52	0.10
4	DCM+2-B/1:4	3.45	8.9%	1.81	4.7%	8.16	26.6%	77.6	64.4	89.1	74.3	1.91	0.42
5	DCM+2-B/1:1	4.49	39.0%	2.35	21.0%	15.87	160.3%	81.8	70.2	94.1	74.0	1.91	0.28
6	DCM+2-B/4:1	2.53	1.5%	1.03	1.7%	20.50	0.0%	71.7	50.8	95.3	73.8	2.45	0.12
7	2-B +THF/1:4	3.78	4.4%	2.19	2.4%	7.90	14.1%	79.1	68.7	88.8	74.2	1.73	0.48
8	2-B +THF /1:1	3.48	5.3%	2.05	1.2%	7.10	10.3%	77.7	67.2	87.7	74.1	1.70	0.49
9	2-B +THF /4:1	2.76	6.7%	1.72	6.7%	5.63	11.5%	73.4	63.3	84.9	73.9	1.60	0.49

Table A-3. P_{HMF}, P_{LVA}, P_{FF}, separation factors and purification of 5-HMF after extraction with 20wt% NaCl at pH 2.0

Entry No.	Organic solvent	P_{HMF}	Stedv. of P_{HMF}	P_{LVA}	Stedv. of P_{LVA}	P_{FF}	Stedv. of P_{FF}	R_{HMF} (%)	R_{LVA} (%)	R_{FF} (%)	Purity of 5-HMF (%)	S_1	S_2
1	DCM+THF/1:4	4.35	1.1%	2.69	5.0%	15.67	109.6%	81.3	72.9	94.0	83.2	1.62	0.28
2	DCM+THF /1:1	3.58	0.4%	1.78	7.9%	18.69	98.6%	78.2	64.0	94.9	82.9	2.01	0.19
3	DCM+THF/4:1	2.44	1.3%	1.11	1.5%	22.13	72.1%	71.0	52.6	95.7	82.0	2.21	0.11
4	DCM+2-B/1:4	5.13	2.7%	1.91	40.0%	12.34	113.8%	83.7	65.6	92.5	84.1	2.69	0.42
5	DCM+2-B/1:1	5.47	5.6%	1.62	12.6%	18.70	54.7%	84.5	61.8	94.9	84.1	3.38	0.29
6	DCM+2-B/4:1	4.02	0.4%	1.73	5.1%	27.56	105.7%	80.1	63.4	96.5	83.1	2.32	0.15
7	2-B +THF/1:4	4.89	0.8%	4.82	8.3%	13.42	44.0%	83.0	82.8	93.1	83.2	1.01	0.36
8	2-B +THF /1:1	5.30	1.5%	3.54	7.5%	11.49	42.4%	84.1	78.0	92.0	83.7	1.50	0.46
9	2-B +THF /4:1	3.62	3.2%	2.39	24.2%	8.01	27.4%	78.3	70.5	88.9	83.4	1.51	0.45

Table A-4. Solvent recovery rate with 20wt% NaCl at pH 2.4

Entry No.	Organic solvent	Vorg (mL)	Vaq (mL)	Total volume (mL)	Solvent recover rate
1	DCM+THF/1:4	2.30	2.60	4.90	92.0%
2	DCM+THF /1:1	2.25	2.30	4.55	90.0%
3	DCM+THF/4:1	2.40	2.25	4.65	96.0%
	Group 1 Average	2.32	2.38	4.70	92.7%
4	DCM+2-B/1:4	2.25	2.45	4.70	90.0%
5	DCM+2-B/1:1	2.05	2.45	4.50	82.0%
6	DCM+2-B/4:1	2.30	2.25	4.55	92.0%
	Group 2 Average	2.20	2.38	4.58	88.0%
7	2-B +THF/1:4	2.40	2.40	4.80	96.0%
8	2-B +THF /1:1	2.40	2.45	4.85	96.0%
9	2-B +THF /4:1	2.30	2.55	4.85	92.0%
	Group 3 Average	2.37	2.47	4.83	94.7%

Table A-5. Solvent recovery rate with 10wt% NaCl at pH 2.4

Entry No.	Organic solvent	Vorg (mL)	Vaq (mL)	Total volume (mL)	Solvent recover rate
1	DCM+THF/1:4	2.15	2.65	4.80	86.0%
2	DCM+THF /1:1	2.35	2.35	4.70	94.0%
3	DCM+THF/4:1	2.20	2.15	4.35	88.0%
	Group 1 Average	2.23	2.38	4.62	89.3%
4	DCM+2-B/1:4	2.30	2.40	4.70	92.0%
5	DCM+2-B/1:1	2.10	2.45	4.55	84.0%
6	DCM+2-B/4:1	2.30	2.30	4.60	92.0%
	Group 2 Average	2.23	2.38	4.62	89.3%
7	2-B +THF/1:4	2.45	2.40	4.85	98.0%
8	2-B +THF /1:1	2.40	2.35	4.75	96.0%
9	2-B +THF /4:1	2.45	2.45	4.90	98.0%
	Group 3 Average	2.43	2.40	4.83	97.3%

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