CATALYTIC CONVERSION OF WASTE WATER FROM STARCH INDUSTRY TO γ -VALEROLACTONE

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A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
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for the Degree of Master of Engineering
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ABSTRACT

γ-valerolactone (GVL) is considered to be one of the most attractive molecules from the derivative of levulinic acid, which can be efficiently used as solvent, liquid fuel, fuel additive and precurser for several novel polymers or alkanes. In this present work, levulinic acid was firstly produced by dehydration and rehydration of sugar-rich wastewater containing H_2SO_4 from starch industry. This study proposed feasibility of utilizing waste water that obtained from nano-crystalline process of starch factory as resource for the production of levulinic acid without catalyst adding. The highest yield of levulinic acid obtained from wastewater was 91.41 mol % at 140 °C with the reaction time of 240 min. As the next step, extraction and reactive extraction were employed to separate levulinic acid from aqueous mixtures contained H_2SO_4. The highest extraction efficiency of levulinic acid from the aqueous mixtures containing the high acid concentration (H_2SO_4) by using 2-sec-butylphenol as extractant at 25 °C was about 70.0 %. For reactive extraction, the conversion of levulinic acid and yield of 2-buthyl levulinate ester were 87.04 % and 75.03 % by mol, respectively. Lastly, the possibility of production GVL from levulinate ester via catalytic tranfer hydrogenation was examined. The highest yield of GVL was 100% mol at 100 °C under 10 bar of nitrogen atmosphere.

Keywords: wastewater, renewable, levulinic acid, levulinate ester, γ-valerolactone

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CHAPTER 1
INTRODUCTION

1.1 Rationals

At present, crude oil is the main source of energy and various petrochemical-based organic chemical products in the world. Almost all modern products in the 21st century, such textile, lubricant, resin, polymer, fertilizers and asphalt, are also derived from crude oil. Furthermore, the demand for crude oil is expected to increase as a result of population and economic development. Which against to crude oil supply, it is perspective depletion. This raises serious issues about the balance of energy markets, as well as the raising price of fossil fuel. In addition, the world is concerned about high emissions from crude oil, which cause global warming problem. Due to those reasons, development of green and sustainable technologies for bulk chemical and fuel productions are highly of interest.

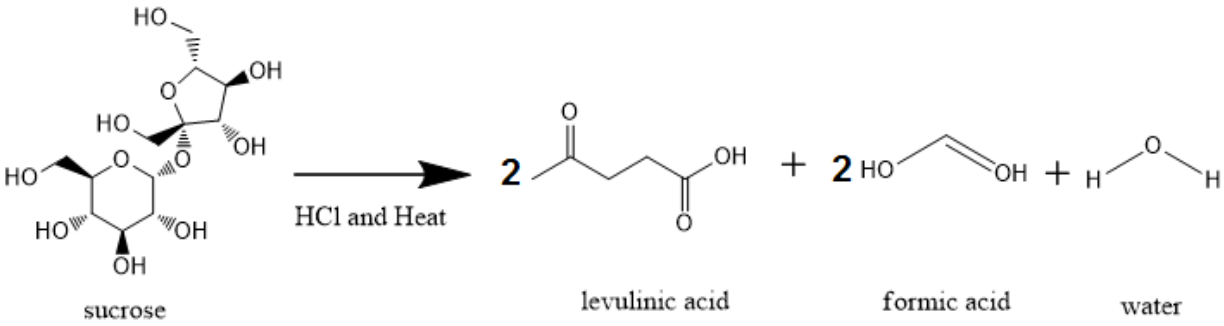
One of the most interesting alternative feedstocks is sugar derived from biomass, because biomass is an abundant carbon source in nature which can be converted via many processes such as mechanical, biological, and thermal processes to several energy forms and valuable chemicals. Generally, biomass composes of cellulose, hemicellulose and lignin. Recently, the production of biofuels and chemicals from biomass via bio-refinery concept has been developed worldwide [1]. Examples are the production of organic acids from hexose via thermo-chemical process. levulinic acid (LA) is the well knows examples of organic acid with excellent potential for production of conventional liquid fuel. levulinic acid has been identified as part of promising top-twelve building blocks from lignocellulosic biomass [2], as result of two reactive functional group, ketone and carboxylic that consists in molecule. In addition, levulinic acid is also versatile building blocks chemical for numerous industrial applications [3-5]. It has been employed as a precursor for the production of 5-methyl-2-pyrrolidone, diphenolic acid, δ-amino levulinic acid, succinic acid, γ-valerolactone, butanone, pyrrolidones, methyl vinyl ketone, methyltetrahydrofuran, levulinate esters, diesel, gasoline, and jet fuel etc.

Conventionally, levulinic acid is produced from sugar derived from biomass via acid catalyzed degradation of hexose by using a mineral acid as the catalyst. The information from previous studies [6-10] indicated that the production of LA react through 2 steps, firstly dehydration of hexose to 5-hydroxymethyl-furfural (HMF) which is intermediate product and subsequently hydrated in second step to form levulinic acid [11]. The conventional method for produced levulinic acid is necessary to separation process for remove mineral acid from production product because mineral acid badly affects the downstream process. The separation process is an energy-intensive process that involves solvent extraction and distillation. The utilization of the products form degradation of hexose with acid catalyst to produce γ-valerolactone (GVL) which eliminated separation process will make the process more worthy in commercial scale. The γ-valerolactone (GVL) obtained from hydrogenation of levulinate ester. It is a versatile precursor for the production of alkanes and valuable chemicals.

1.2 Literature Review

1.2.1 Production of levulinic acid from sugar

The first report on the production of levulinic acid is by Mulder et al [12], who synthesized it by heating sucrose with hydrochloric acid at high temperature. The reaction occurs by sucrose cleavage and dehydration to give levulinic acid, formic acid and water as shown in Scheme 1.



Scheme 1.1 Synthesis of levulinic acid from sucrose

Tarabanko et al [13] studied the influence of different sugars (sucrose, glucose and fructose) and nature of acid catalyst on the production of levulinic acid at moderate temperature. The acid catalysts which used in this work were HCl, H_2SO_4 and H_3PO_4. The results showed that sucrose and fructose gave relatively high levulinic acid formation, while glucose produced lower yield of levulinic acid as shown in Figures 1.1. The influence of reaction temperature at moderate temperature is shown in Figures 1.2, from which the yield and reaction rate of levulinic acid formation increased with the rising reaction temperature. In addition, it was found that raising HCl concentration slightly affected the rate of levulinic acid formation. The influence of acid types on the kinetics of levulinic acid formation at constant H° is presented in Figure 1.3. Clearly, the selectivity of levulinic acid formation by using HCl as catalyst are higher than H_2SO_4.

In addition, the selectivity and rate of levulinic acid formation by using H_3PO_4 as a catalyst is the lowest.

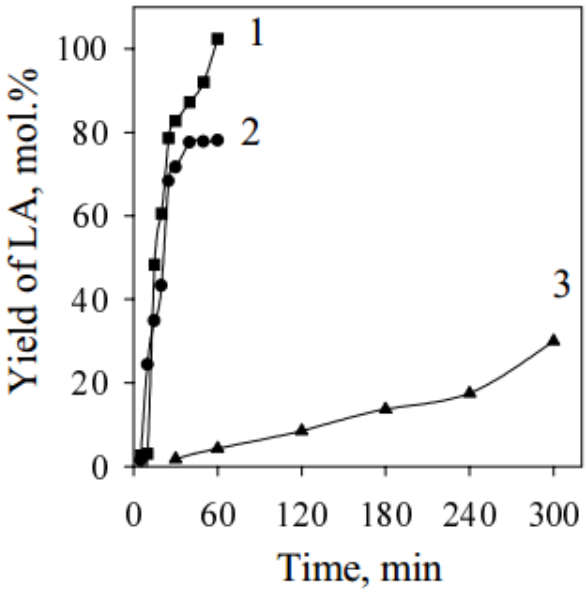


Figure 1.1 Kinetic curves of levulinic acid production from sucrose(1), fructose(2) and glucose(3) [13].

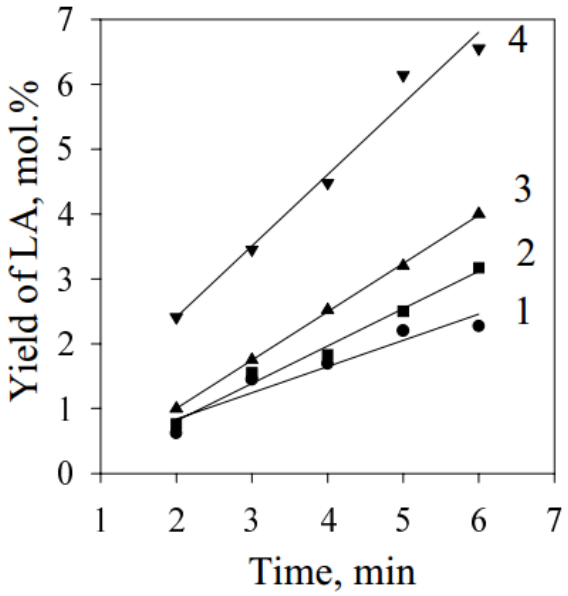


Figure 1.2 Kinetic curves of levulinic acid formation from 0.25 M glucose and 4.125 M HCl at different temperatures (85.0 °C (1), 87.2°C (2), 90.0 °C (3) and 92.5 °C (4))[13].

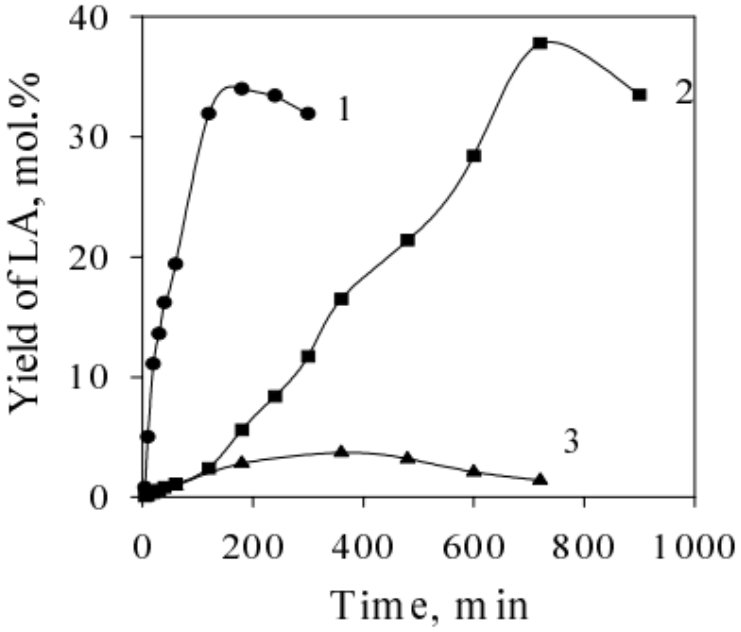


Figure 1.3 Kinetic curve of levulinic acid formation from 0.35M glucose at 98°C and H^o= -2.6 which (1)7.2 M HCl, (2)5.8 M H_2SO_4, (3)10 M H_3PO_4)[13].

Girisuta et al. [14] developed a kinetic scheme for the conversion of glucose by using H_2SO_4 as the catalyst to levulinic acid by including the kinetics of byproduct formation and incorporation of HMF as an intermediate. That work also investigated the influences of temperature, glucose concentration and acid concentration on levulinic acid formation. The experiments were carried out in various temperatures (140-200°C), initial concentration (0.1-1.0 M) and using H_2SO_4 as catalyst (0.05-1M). In all experiments, it was observed that HMF and humin are generated as by-product. Nevertheless, the maximum concentration of HMF was usually less than 5%. This observation indicated that the rate of HMF formation is lower than rate of levulinic acid formation. The rate of glucose decomposition increased with raising the reaction temperature, but the selectivity and maximum yield of levuinic acid formation decreased with raising reaction temperature as shown in Figure 1.4. The effect of glucose concentration and time on the yield of levulinic acid is presented in Figure 1.5, which indicates lower initial concentration of glucose and high yield of levulinic acid that increases with increasing reaction time. Furthermore, the concentration of H_2SO_4 strongly affected the rate of levulinic acid formation from glucose, but slightly affected the yield of levulinic acid as shown

in Figure 1.6. The maximum yield of levulinic acid production from this process was 60% mol at C_{GLC} = 0.1 M, $C_{H_2SO_4} = 1M$, and T=140°C.

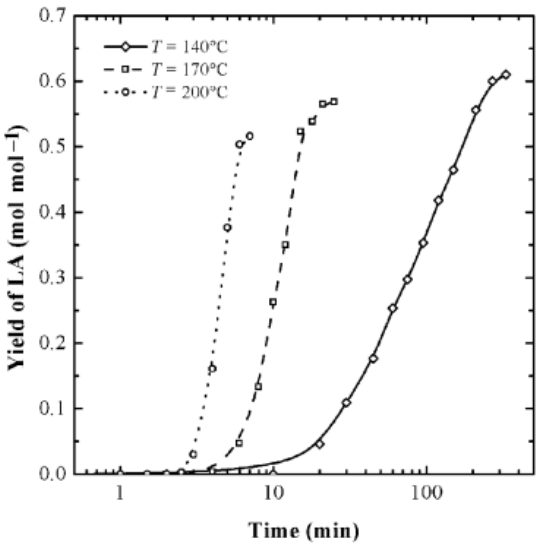


Figure 1.4 Influence of reaction temperature on levulinic formation at $C_{glu} = 0.1M$, $C_{H_2SO_4} = 0.5M$ [14]

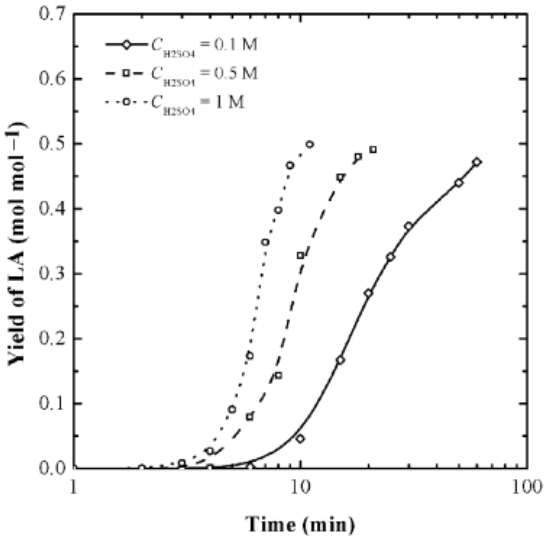


Figure 1.5 Influence of glucose concentration on levulinic formation at T=140°C, $C_{H_2SO_4} = 1M$ [14]

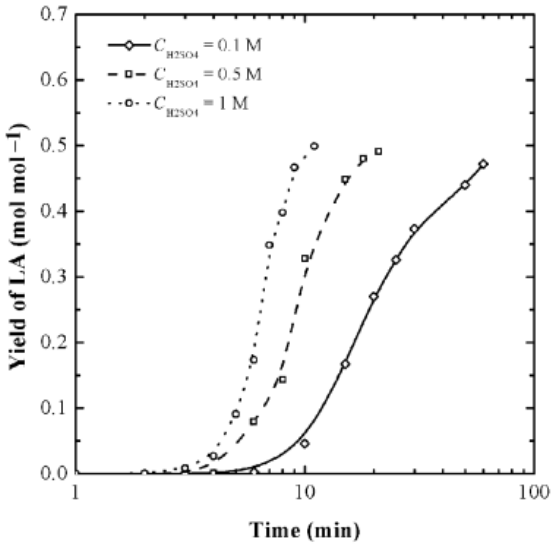


Figure 1.6 Influence of H_2SO_4 concentration on the yield of levulinic acid at T=170°C, $C_{GLC_0} = 0.5M$ [14]

Chang et al. [15] studied the kinetics of levulinic acid formation from glucose by using H_2SO_4 as the catalyst at temperature above 160 °C. The experiments were performed at temperatures of 170 °C, 190 °C and 210 °C with concentration of H_2SO_4 between 1-5%.The influences of reaction temperature and concentration of acid catalyst on levulinic acid formation are shown in Table 1.1. It can be seen that the kinetic constant of glucose decomposition is higher than the kinetic constant of HMF in every experiments indicating that some part of glucose converted to by-product (i.e. humin) and the yield of levulinic acid cannot achieve its theoretical yield. The glucose decomposition and HMF formation rate constant (k) is a function of reaction temperature and acid concentration. The rate constant of glucose decomposition (k), HMF formation (k_1) and levulinic acid formation (k_2) increased with the raising of acid concentration at constant temperature. The rate constant of HMF formation (k_1) and levulinic acid formation (k_2) increased with the raising of reaction temperature but yield and selectivity of levulinic acid formation decreased with raising of reaction temperature. The rate constant of humin formation is a function of temperature but it is not a function acid concentration. These results conclude that higher reaction temperature results in lower yield of levulinic acid. That work also reported activation energy for the HMF formation of 86.33 kJ.mol^{-1}, levulinic acid formation of 56.95 kJ.mol^{-1} and humin formation of 209.5 kJ.mol^{-1}.

Table 1.1 Kinetic parameters for the acid decomposition of glucose; k is kinetic constant of glucose decomposition, k_1=kinetic constant of HMF formation from glucose, k_2 is kinetin constant of levulinic acid formation from HMF and k_3 is kinetic constant of humin formation from glucose [15].

T, ℃	Acid concentration, %	k, min^{-1}	k_1, min^{-1}	k_2, min^{-1}	k_3, min^{-1}	k_1/k	k_2/k
170	1	0.0566	0.0458	0.1018	0.0108	0.8092	1.7986
	3	0.0845	0.0605	0.2382	0.024	0.7160	2.8189
	5	0.0964	0.0837	0.3170	0.0127	0.8682	3.2884
190	1	0.2939	0.1089	0.1230	0.185	0.3705	0.4185
	3	0.2924	0.1734	0.4382	0.119	0.5930	1.4986
	5	0.4875	0.2537	1.0510	0.232	0.5204	2.155
average activation energy, $kJ \cdot mol^{-1}$			E_1	E_2	E_3		
			86.33	56.95	209.5		

Jing at el. [16] developed a kinetic equation for glucose decomposition in high-temperature liquid water (HTLW) from 180 to 220 ℃ at pressure of 10 MPa. The influence of reaction time and reaction temperature on the process and stability of levulinic acid in HTLW at temperature between 220 to 260℃ were also investigated. They reported that HMF and levulinic acid are the main products from glucose decomposition in HTLW. The results also showed that rate of glucose conversion and yield of levulinic acid are function of reaction time and reaction temperature. The rate of glucose conversion and yield of levulinic acid promoted with rising reaction temperature and reaction time. The yield of HMF increased with raising temperature from 180 to 200 ℃ but when temperature higher than 200 ℃, yield of HMF increased initially before dropping down. The highest yield of HMF was 32.0% mol after 30 min reaction time at 220 ℃. The results form stability test of levulinic acid conversion in the HTWL indicated that the maximum levulinic acid decomposition was only 7.08% at 280℃ for 32 h, then it turned to be stable under the experimental condition. The evaluated activation energy from their experiment were 118.85, 95.40, and 31.29 $kJ.mol^{-1}$ for the decomposition of glucose, 5-HMF, and LA, respectively.

1.2.2 Production of γ-valerolactone (GVL)

Even though using homogenous mineral acids such as H_2SO_4 or HCl as catalyst for the production of levulinic acid results in the highest yield of levulinic acid production, it is necessary to separate the product from the reactant and the mineral acid, which is the major drawback for the downstream process. The costs of separation, purification and neutralization steps for the process using homogeneous mineral acid as catalyst are relatively expensive. These reasons have driven research towards the use of reactive extraction for converting levulinic acid to γ –valerolactone.

Alonso et al. [17] studied the influence of using GVL as a solvent on the process that used solid acid catalyst for converting cellulose to levulinic acid and GVL. The reactions for producing levulinic acid from cellulose were performed with various type of solid catalyst by using pure water or using 10 wt% of GVL in water as solvents. Table 1.2 shows that yield of levulinic acid and formic acid from the process that using pure water as solvent lower than yield of levulinic acid and formic acid from the process that used GVL/water as solvent. In the GVL/water systems, humin was not observed from reaction, whereas this compound can be observed in reaction that using water as solvent, indicating that GVL effectively solubilizes humin. The maximum yield of Levulinic acid is 69% mol after 16 h of reaction time, which can be achieved by using Amberlyst 70 with GVL/water as solvent. The increasing of levulinic acid formation when using the GVL/water systems as solvent explain by the solubilization of cellulose with GVL, then interaction between sugar oligomer and acid site can be promoted. In addition, GVL also improved the diffusivity through the pores which promoted catalytic activity. It was also observed that increasing proportion of GVL in the GVL/water systems results in the rising of reaction rates and yields until proportion of GVL more than 90 % wt, then the overall yield drops with increasing while the reaction rate still increases. Since levulinic acid was produced through rehydration reaction of HMF, it requires water in this process. The yields of levulinic acid and formic acid increased with reaction time.

Table 1.2 Influence of acid catalyst and solvent on the yield of Levulinic acid and formic acid. Reaction conditions: 2% of cellulose, 433 K, 0.2 g catalyst, 3 mL of solvent (purewater or 90 wt% GVL/10 wt% water) [17].

	Yield (%)							
	100 wt% water				90 wt% GVL/10 wt% water			
	4 h		16 h		4 h		16 h	
Catalyst	FA	LA	FA	LA	FA	LA	FA	LA
Blank	0	0	0	0	2	0	0	0
0.05 M SA	9	5	41	36	59	63	32	59
0.005 M SA	2	0	4	1	35	40	49	59
Amberlyst 70	6	3	25	19	53	59	20	69
Nafion SAC13	3	1	9	6	36	47	49	63
C–SO_3H	15	4	48	20	35	39	22	56
Propylsulfonic (silicycle)	20	14	60	53	54	54	35	55
Tosic (silicycle)	12	8	65	55	55	51	12	47
ZSM-5	2	0	8	2	0	17	12	35
Mordenite	2	0	6	2	0	20	19	35
Nb_2O_5	4	0	4	1	0	20	0	25
Silica–alumina	0	0	0	0	0	15	0	7
0.05 M SA[a]	13	6	41	28	41	38	5	43
Amberlyst 70[a]	20	10	33	23	48	46	31	54

[a] Corn stover equivalent to 2 wt% cellulose (~6 wt%) was used as the feed.

Figure 1.7 shows that the yield of levulinic acid decreases with increasing number of reutilized catalyst. At 4 time of reutilized, yield of levulinic acid incrementally decreased from 58% to 27% due to the formation of humin on the Amberlyst 70. However, the activity of catalyst can be recuperated by washing with a 28.5 wt% of H_2O_2 solution for overnight at room temperature. Gürbüz et al [18] applied reactive extraction and dual-catalyst for the production of GVL via levulinic acid through hydrogenation process. The levulinic acid obtained from catalystic decomposition of cellulose at 423 K by using sulfuric acid. This work utilized butene to reacting with levulinic acid and Formic acid by using H_2SO_4 as catalyst to produced hydrophobic esters with is automatically separate from H_2SO_4, thereby allowing for recycle of H_2SO_4. The excess butene separates spontaneously from the hydrophobic esters by decreased the pressure of reaction. The dual-catalyst composed with Pd/C and a Ru/C. Formic acid and formate ester were decomposed over Pd/C to produce H_2 and CO. levulinic ester and levulinic

acid were hydrogenated over Ru/C to produced GVL. The overview of the process for reactive extraction of levulinate esters and conversion to GVL is shown in Figure 1.8.

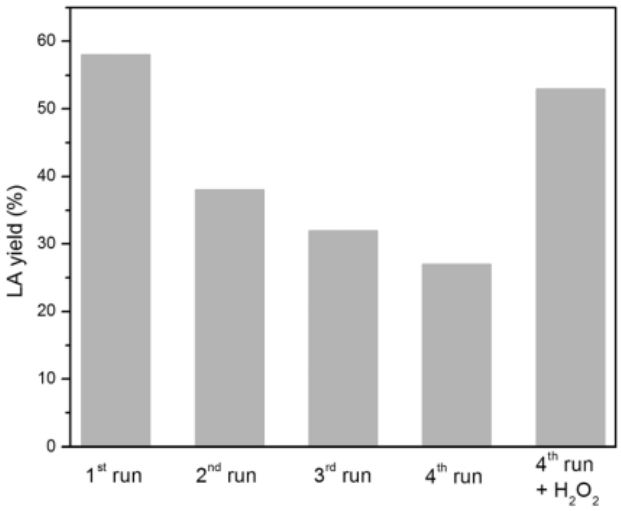


Figure 1.7 The influence of reused Amberlyst 70. Reaction condition : 2 h at 433 K using (90 wt% GVL)/(10 wt% water) as solvent, 2 wt% cellulose and 6 wt% catalyst [17]

The influences of aqueous phase concentrations, temperatures, and reaction times on Levulinate ester formation are shown in table 1.3. Increasing concentration of Levulinic acid and H_2SO_4 results in raising the yields of butyl levulinate, then higher amount of water in system leads to decreasing the yields of butyl levulinate. Rising reaction temperature results in decreased the yields of butyl levulinate and the amount of H_2SO_4 recovered, but leads to increasing degradation products. The rate of GVL production over Ru/C significantly increased with adding water with butyl levulinate.

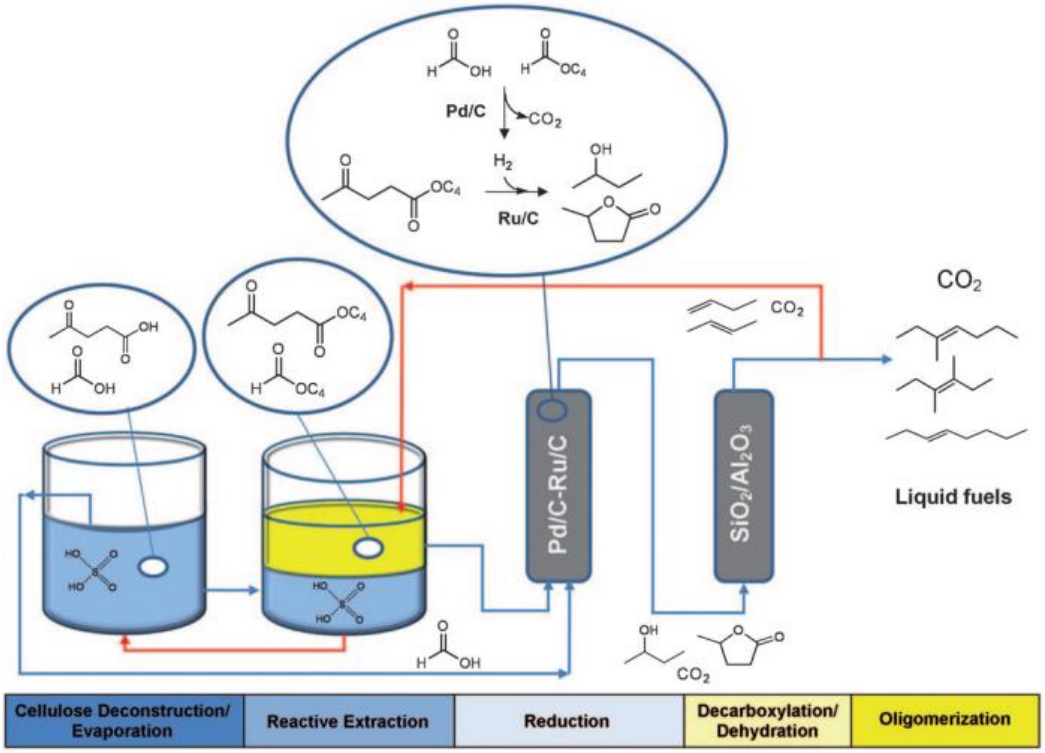


Figure 1.8 Overall view of GVL production via Levulinic acid by using dual catalyst system[18].

Table 1.3 Effects of aqueous phase concentrations, temperatures, and reaction times on the yield of sec-butyl levulinate (BL) and sec-butyl formate with different. (Butene: Levulinic acid molar ratio is equal to 5:1)

Entry	T [K]	t [h]	Feed [M] LA	FA	H_2SO_4	H_2O	Conversion LA [%]	Yield [%] BL	LA org[a] [%]	LA aq[a] [%]	H_2O [g g^{-1} LA]	H_2SO_4 aq [M]
1	403	16	2	0	0.5	40	0	0	0	100	-	-
2	353	2	8	0	2	4.5	91	85	2	7	5	0.4
3	333	4	8	0	2	4.5	86	78	2	12	5	0.4
4	403	2	8	0	2	4.5	85	73	3	12	5	0.4
5	373	2	8	0	2	4.5	91	82	2	7	5	0.4
6	353	2	4	0	1	30	0	0	0	100	-	-
7	353	2	6.4	0	1.6	16.5	55	48	5	40	6	0.4
8	353	2	6.3	2.3	1.6	11.3	84 (48)[c]	78 (43)[c]	5 (28)[c]	11 (24)[c]	1	1.5
9[b]	353	12	6.3	2.3	1.6	11.3	60 (49)[c]	59 (47)[c]	20 (27)[c]	20 (24)[c]	1	1.6

[a] The percentages are calculated based on LA in the initial feed. Partition coefficient ($M_{org}/M_{aq} = 1$). [b] Butene:LA molar ratio is equal to 2:1. [c] Refer to FA/BF.

Manzer et al. [19] studied the hydrogenation of levulinic acid by using various supported metal catalysts. The experiments were performed by using Ir, Rh, Pd, Ru, Pt, Re and Ni as the active metal on a carbon support in dioxane at temperature of 150 °C, reaction time of 120 min, and 55 bar. The results indicated that the Ru, Ir, Rh and Pd were active but only Ru achieved high yield of GVL. Yang et al.[20] studied the catalytic transfer hydrogenation for convert ethyl levulinate to GVL with various catalysts and using secondary alcohol as hydrogen resource. The experiments were performed by using a variety of Ni based catalysts such as Ni/TiO_2, Ni/SiO_2, Ni/CeO_2, Ni/C and RANEY Ni. The results are shown in Table 1.4 (Entry 1-5), from which only RANEY Ni had catalytic activity on this process. Almost ethyl levulinate converted to GVL at 80°C for 9 h. The noble base catalyst such Au/C, Pd/C, Pt/C and Ru/C were performed in catalytic transfer hydrogenation process for compare with RANEY Ni. The reaction with Ru/C catalyst results in higher yield of GVL than other noble base catalyst as shown in Table 1.4 (Entry 6-9). The active catalysts for catalytic transfer hydrogenation were also tested at room temperature, from which only RANEY Ni showed high catalytic activity (Entry 10-12).

Table 1.4 Influence of catalyst on GVL formation

Entry	Catalysts	T [°C]	Solvent	Yield (%)
1	Ni/TiO_2	80	2-PrOH	0
2	Ni/SiO_2	80	2-PrOH	0
3	Ni/CeO_2	80	2-PrOH	0
4	Ni/C	80	2-PrOH	1
5	RANEY® Ni	80	2-PrOH	>99
6	Au/C	80	2-PrOH	0
7	Pd/C	80	2-PrOH	1
8	Pt/C	80	2-PrOH	32
9	Ru/C	80	2-PrOH	93
10	RANEY® Ni	r.t.	2-PrOH	>99
11	Pt/C	r.t.	2-PrOH	1
12	Ru/C	r.t.	2-PrOH	27
13[b]	RANEY® Ni	r.t.	2-PrOH	87
14[c]	RANEY® Ni	r.t.	2-PrOH	69
15[d]	RANEY® Ni	r.t.	2-PrOH	95
16[e]	RANEY® Ni	r.t.	2-PrOH	87
17[f]	RANEY® Ni	r.t.	2-PrOH	57/68

[a] 1 mmol EL, catalyst (5 wt%) 30 mg, RANEY® Ni (freshly prepared and kept in 2-PrOH, wet, 0.1 g), room temperature, Ar. The yield was determined by GC using diethylene glycol dimethyl ether as the internal standard. [b] Reaction time 2 h. [c] In air. [d] The catalyst was kept in 2-ProH for 1 week before use. [e] Freshly prepared catalyst and kept in water. [f] RANEY® Ni slurry in water, purchased from TCI/Aladdin.

The reaction time slightly affected GVL production, from which the reducing of reaction time from 8 h to 2 h resulted in the decreasing yield of GVL to 87% mol. The RANEY Ni catalyst was sensitive with air and water. The influence of hydrogen donor for catalytic transfer hydrogenation was investigated. The reactions were performed by using various primary and secondary alcohols as the H-donors and the results are shown in Table 1.5. Among these H-donors, only secondary alcohols achieved high yield of GVL while primary alcohols were low performance as H-donor. The reaction with cyclohexanol also gave low performance.

Table 1.5 Influence of H-donor on the yield of GVL.

Entry	Solvent	GC yield (%)
1	—	18
2[b]	—	1
3	MeOH	24
4	EtOH	27
5	1-PrOH	28
6	2-BuOH	92
7	Cyclohexanol	35
8	2-PrOH	99

[a] Reaction conditions: EL (1 mmol), RANEY® Ni (freshly prepared and kept in 2-PrOH, wet, 0.1 g), solvent (2 ml), room temperature, Ar, 9 h. [b] The catalyst for the second run from entry 1. The yield was determined by GC using diethylene glycol dimethyl ether as the internal standard.

1.3 Research objectives

Firstly, this research aims to investigate the possibility of utilizing waste water from nano-crystalline starch production processes as the raw material for levulinic acid production. Next, extraction and reactive extraction to separate levulinic acid from acid waste are performed. Lastly, this research studies the possibility of applying catalytic transfer hydrogenation for production of GVL from alkyl levulinate ester.

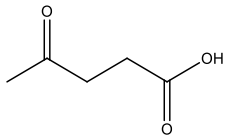
1.4 Scope of research work

- To investigate the influence of glucose's content, reaction temperature and reaction time on the formation of Levulinic acid.
- To investigate the influence of reaction time, reaction temperature, reaction pressure, Raney and levulinate ester on the formation of GVL.
- To optimize the operating conditions where conversion and product selectivity can be maximized.

CHAPTER 2
THEORIES

2.1 Levulinic properties and synthesis routes

Levulinic acid (LA), or 4-Oxopentanoic acid is renewable fix carbon with a low molecular weight fatty acid that is composed with carbonyl and carboxylic group (Scheme 2.1). Both functional groups that contained in molecule of LA leads this compound to be a versatile building block for the synthesis of several organic chemicals [21, 22]. Table 1 shows typical properties of LA.

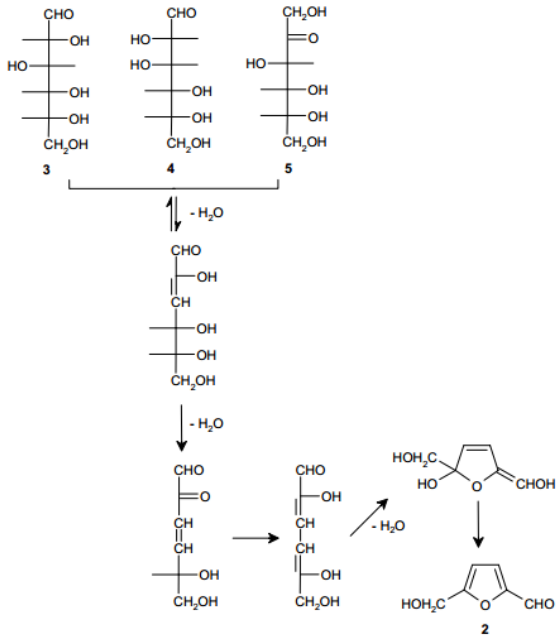


Scheme 2.1 Structure of Levulinic acid

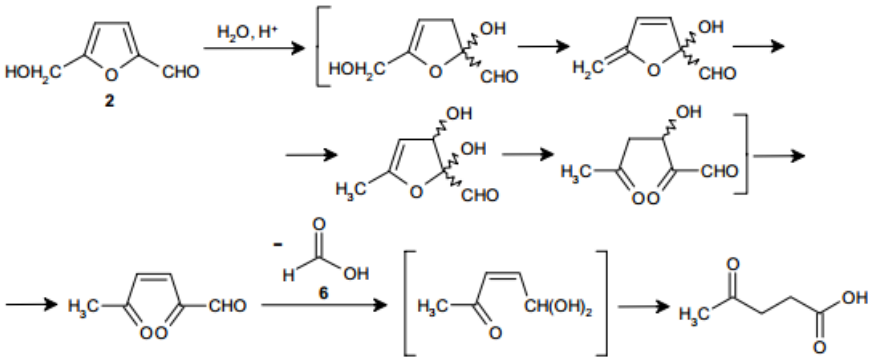
Table 2.1 Typically properties of LA

Properties	**Values**
Boiling Point [K]	513.38
Melting Point [K]	356.14
Critical Temperature [K]	694.71
Critical Pressure [Bar]	41.84
Critical Volume [cm^3/mol]	345.5
Gibbs Energy [kJ/mol]	-481.61
pKa	4.59
Henry's Law	7.7
Heat of Form [kJ/mol]	-609.38
Refractive index at 20 °C	1.1447
Surface tension at 25 °C [dyne cm^{-1}]	39.7

Schemes 2.2-2.3 show the proposed mechanism for the conversion of hexose to HMF following by convert to LA respectively. The theoretical yield of LA from hexose is 100 mol% or 64.5 wt% as a result of co-production formic acid. Generally, LA yield is less than theoretical value about one of third, which because of an undesired side reaction that causing formation of humin which is back insoluble-solid product. Table 2.2 presents an overview of LA production by using various types of feedstock and catalysts.



Scheme 2.2 Dehydration reactions of hexose to HMF [23, 24]



Scheme 2.3 Rehydration reactions of HMF to LA.[25]

Conventionally, levulinic acid is produced from biomass via acid catalyzed degradation of hexose by using mineral acid as the catalyst. The information from previous studies[6-10] hint the production of LA react through 2 steps ,firstly dehydration of hexose to 5-hydroxymethyl-furfural (HMF) which is intermediate product and subsequently hydrated in second step to form LA [11]. Figure 1 and 2 shows the proposed mechanism for the conversion of hexose to HMF following by convert to LA respectively. The theoretical yield of LA from hexose is 100 mol% or 64.5 wt% as a result of co-production formic acid. Generally, LA yield is less than theoretical value about one of third, which because of an undesired side reaction that causing formation of humin which is back insoluble-solid product. Table 2 indicated an overview of LA production by using various types of feedstock and catalysts

Table 2.2. An overview of LA production by using various types of feedstock and catalysts [11].

Reactant	C_i (%w/w)	Catalyst	C_{acid} (%w/w)	Temperature (^oC)	Time (h)	Y_{LA} (%w/w)	Ref
Cane sugar	28	HCl	18	100	24	15	[26]
Corn starch	29	HCl	6.5	162	1	26	[27]
Sucrose	29	HCl	6.5	162	1	29	[27]
Glucose	29	HCl	6.5	162	1	24	[27]
Fructose	29	HCl	6.5	162	1	25	[27]
Corn starch	33	HCl	1.8	200	0.5	35	[28]
Rice hull	14	HCl	1	160	3	10.3	[29]
Rice straw	14	HCl	1	160	3	5.5	[29]
Corn stalks	14	HCl	1	160	3	7.5	[29]
Cotton linters	14	HCl	1	160	3	7.4	[29]
Sucrose	6	H_2SO_4	9	125	16	30	[30]
Sucrose	6	HCl	9.7	125	16	43	[30]
Sucrose	6	H_2SO_4	9	125	16	50	[30]
Pulp slurry	10	HCl	6	160	1	40.5	[31]

Feedstock	C_i (%w/w)	Catalyst	C_{acid} (%w/w)	Temperature (^oC)	Time (h)	Y_{LA} (%w/w)	Ref
Glucose	10	HCl	6	160	0.25	41.1	[31]
Fructose	50	LZY-zeolite	50	140	15	43.2	[32]
Glucose	12	Cray catalyst	3	150	24	12	[33]
Glucose	12	HY-zeolite	3	150	24	12	[34]
Cellulose	10	H_2SO_4	3	250	2	25.2	[35]
Cellulose	10	H_2SO_4	1-5	150-250	2-7	≤25.2	[36]
Cellulose	10	HCl	1-5	150-250	2-7	≤28.8	[36]
Cellulose	10	HBr	1-5	150-250	2-7	≤26.9	[36]
Aspen wood	10	H_2SO_4	1-5	150-250	2-7	≤15.5	[36]
Aspen wood	10	HCl	1-5	150-250	2-7	≤12.4	[36]
Aspen wood	10	HBr	1-5	150-250	2-7	≤13.0	[36]
Newspaper	30	H_2SO_4	10	150	8	12.5	[37]
Sorghum	10	H_2SO_4	8	200	0.67	32.6	[37]
Extrude starch	25	H_2SO_4	4	200	0.67	47.5	[38]
Wheat	6.4	H_2SO_4	3.5	209.3	0.63	1.98	[39]

2.2 Potential applications of LA and its derivatives

LA has been identified as part of promising top-twelve building blocks from lignocellulosic biomass[2], as a result of two reactive functional groups, ketones and carboxylic acid that consists in molecules.

The esterification reaction at carboxylic group is one of important reaction for LA with potential to produce various levulinate ester. The previous studies[40-42] show the esterification reaction with presence acid such as sulfuric acid or polyphosphoric acid obtained higher yield of levulinate ester. A research by Tecaxo and Biofine Inc[43] indicate that Ethyl levulinate, a product from esterify of LA, can be used as an oxygenate additive in regular diesel engine with ratio 20% Ethyl levulinate ,1% of co-additive and 79% diesel.

The oxidation reaction of LA produced various flexible derivatives that depend on the reaction type of the oxidant agent. For example, LA can be converted to succinic acid, a versatile compound for agrochemicals, pharmaceuticals and polymer application, with a typical yield of about 80% by using V_2O_5 as catalyst in present of oxygen at temperature in rang 365–390 °C[44]. The global succinic acid market was valued at USD 240.3 million in 2011 and is expected to reach USD 836.2 million by 2018[45].

LA can be reduced to produce γ-valerolactone (GVL) via catalytic hydrogenation. GVL is an interesting derivative with broad application range, it can be reduce to methyltetrahydrofuran (MTHF) with yield high as 83 mol %[46], and MTHF has potential as a gasoline oxygenate and has a predicted [47] market potential as high as $2.6\times10^5 m^3/year^{-1}$.

Table 2.3 Overview potential of Levulinic acid and its derivatives.

Derivative	Production method	Potential
Levulinate ester	Levulinate esters are mainly produced by esterifying Levulinic acid with alkyl alcohols in the presence of an acid catalyst.	Levulinate esters are the important compound with numerous potential applications in the flavoring and fragrance industry [48-50]. And it can be used as solvents, plasticizers for cellulose plastics [50], octane booster[51] or oxigenate addition for gassoline[52], additive for improve flow of biodiesel at low temperature[53] and additive in diesel with modified to better fuel property such as a clean burning fuel with high. Moreover, levulicante esters can be used as fuel for the direct firing of gas turbines[61]

Derivative	Production method	Potential
diphenolic acid	It is produced through the condensation reaction of levulinic acid with phenol in the presence of an acid catalyst.	Diphenolic acid is a versatile building block for producing various polymers[14, 21, 62-64], fire-retardant materials[65, 66], paints or coating material[67] and lubricants[68]. In polymer application, it can be directly used for replaces Bisphenol A (market potential as high as 4.5×10^4 Tons/year [21]) as raw material for production of polycarbonates, epoxy resins, polysulfones ,polyether ketones and other polymer[2, 21, 69].
5-methyl-2-pyrrolidone	5-methyl-2-pyrrolidone is produced through reductive amination of Levulenic acid in the presence of metal catalyst.	5-methyl-2-pyrrolidone is a applicable intermediate in the pharmaceutical industry.[70]

Derivative	Production method	Potential
γ-valerolactone (GVL)	The production of γ-valerolactone occurs through the catalytic hydrogenation of Levulinic acid.	γ-valerolactone (GVL) can be used as a substitute for ethanol in gasoline ethanol blends[71], as starting materials for the production of excellent solvents which are renewable, non-toxic and biodegradable[72]. The hydrogenation of GVL can be produced methyltetrahydrofuran, a high molecular weigth hydrocarbon, which have similar properties to gasoline, diesel and jet fuel[73]. Methyltetrahydrofuran can be blended up to 70% into gasoline[74] and has a predicted market potential as high as 2.6×10^5 m^3/year[21]. GVL can be converted to 5-nonanone, which has similar properties to diesel fuel[75]. The GVL can be converted via decarboxylation to produce a butene and carbon dioxide, which butene can be produced alkenes with molecular weights that can be targeted for gasoline and/or jet fuel applications via oligomerization reaction[76]. Moreover, GVL is considered as interesting precursor (or as raw material for co-polymerization[77, 78]) for production of bio-base polymer, which is green polymer[12] such as poly-α-methylene- γ –valerolactone[79], γ-valerolactone-derived thermoset[80].

Derivative	Production method	Potential
Succinic acid	Succinic acid is produced via an oxidation process in the presence of a catalyst at high temperature and using V_2O_5 as a catalyst.	Succinic acid (the estimated market potential based on products is 2.7×10^5 tons/year[81]) is a versatile starting material for produced several valuable chemicals such as γ-butyrolactone with is intermediate for agrochemicals and pharmaceuticals[69], tetrahydrofuran with is a solvent for poly-(vinyl chloride) and starting material for the production of polytetramethylene glycol (It is an intermediate for Spandex fibers and polyurethanes) [82], 1,4-butanediol with is a raw material for production of polybutylene terephthalate ,which used for produce engineering plastics, fibers,films and adhesives[11].

CHAPTER 3
METHODOLOGY

3.1 Materials

The chemicals in this research include glucose, levulinic acid, sulfuric acid, butanol, 2-propanaol, 2-butanol, methyl levulinate**,** ethyl levulinate and γ-valerolactone. All chemicals were commercial grade and used without further purification. The waste water was obtained from nano-crystalline starch production process in starch industrial**.**

3.2 Experimental procedure

3.2.1 Levulinic acid formation

A 500 ml autoclave reactor made of 316L stainless steel was used for this experiment. The reactor was filled with waste water 240 ml at room temperature and deoxidized by bubbling with high purity nitrogen for 30 min. The reactor was placed in a constant temperature oven (±1 ^{o}C with set point). At different reaction temperatures (120-220 ^{o}C) and times (240-360 min), reactors were taken from the oven and quenched into an ice-water bath to stop the reaction. The samples were taken out of the autoclave reactors and filtrated by using a 0.22 μm cellulose acetate filter for separated the insoluble humins from products. The filtrate was subsequently analyzed using High Performance Liquid Chromatography (HPLC). The insoluble humin content was dried in the oven and analyzed with a CHN analyzer for determined composition of humin.

3.2.2 Extraction and reactive extraction of Levulinic acid

The product samples used as the reactants in the separation part were obtained from the hydrothermal of wastewater at reaction temperature of 140 °C for 4 hours of reaction time. For the liquid-liquid extraction of levulinic acid in the aqueous mixtures containing the high acid concentration, the extraction was performed with Methyl isobutyl ketone and 2-sec-butylphenol at 25 °C and various extraction time (1, 2 and 3 hours). The ratio of a mixture between aqueous containing the high acid concentration and organic phase (Methyl isobutyl ketone and 2-sec-butylphenol) is equal to 10:10 by weigh.

For the reactive extraction of Levulinic acid in the aqueous mixtures containing the high acid concentration, the reactive extraction was performed with various types of alcohol (2-propanaol, 1-butanol and 2-butanol) at reaction temperature of 100 °C for 2 hours. The ratio of a mixture between aqueous containing the high acid concentration and alcohol is equal to 10:30 by volume. The product was filled by using a 0.2 mm cellulose acetate filter. The composition of aqueous phase was determined using a HPLC system, while the composition of organic phase was determined using a GC-FID and confirm product with GC-MS.

3.2.3 Pretreatment of RANEY

The RANEY was used in the pretreatment step to obtain high activity at low temperature and low pressure. The pretreatment step was as follows. Firstly, an aqueous solution of NaOH was prepared at concentration of 6.0 M. The 50.0 mL of NaOH solution was controlled temperature in the range of 5-15 ℃. And 10.0 of RANEY (Ni–Al alloy in weight ratio of 50:50) was slowly added to NaOH solution (still control temperature) and the mixture was stirred for 60 minutes. After that, the mixture was raised to room temperature for 30 minutes. Following by heated the mixture to 90℃ and stirred for 16 hours (until no H_2 bubbles). Then the RANEY was washed with deionized water until the pH change to 7 and kept pretreated RANEY in anhydrous 2-propanol.

3.2.4 Production of γ-valerolactone from akly levulinate ester

The experiments on catalytic transfer hydrogenation were carried out in a glass (reflux system) or a pressure reactor at various temperatures. The reflux system composed with a 100 ml of glass round bottom flask equipped with a condenser, which 5 °C of the water was flowed insight, and placed in the oil bath that using thermocouple to measure temperature and controlled temperature with electrical thermostat. The glass round bottom or pressure reactor was filled with methyl levulinate or ethyl levulinate, sec-propanol and pretreated RANEY in the various predetermined ratio at room temperature. The reaction started when the reactor was placed in to preheated oil bath (for reflux system) or placed in to heating jacket (for pressure reactor) at design reaction temperature. 0.1 ml of sample was collected before the reaction started and every hour during the experiment. The collected sample was filled with 0.22 µm cellulose acetate filter to separate the catalyst and quench in ice water for terminated reaction. The 10 µl of sample was

diluted with ethanol to 1.00 ml and subsequently analyzed by Gas Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography with mass spectrometry (GC-MS).

3.2.5 Recyclability of RANEY for the production of γ-valerolactone

The catalytic stability of RANEY from Fluka was appraised by reusing RANEY in the catalytic transfer hydrogenation reaction of methyl levulinate. The condition for the catalytic stability test is 100 °C of reaction temperature in air atmosphere for 3 hours of reaction time. Before reusing Raney for the next experiment, the Raney was washed five times with 30 mL of 2-propanol in each time. The Raney was reused four times under these conditions. The collected sample quench in ice water for terminated reaction and also analyzed with Chromatography with Flame Ionization Detector (GC-FID) and Gas Chromatography with mass spectrometry (GC-MS).

3.3 Analytical method

3.3.1 Determined acid concentration polysaccharide in waste water

The acid (H_2SO_4) concentration of waste water was determined by a titration technique, using NaOH as the titrant. Potassium hydrogen phthalate (KPH) was used as the primary standard for evaluating really concentration of titrant. Phenol red was used as indicator in all analyzes.

To examine the polysaccharide content in wastewater, the acid concentration in the waste water was concentrated to 12.00 M (240 ml) by adding 152.03 ml of 18.00 M H_2SO_4 in to 50.00 ml of waste water and then the concentrated waste water was carried out in oven at 60 ℃ for 4 hours. At a designed temperature, the samples were taken out of the autoclave reactors and analyzed using High Performance Liquid Chromatography (HPLC).

3.3.2 Determined concentration products sample with HPLC system.

The concentrations of glucose in waste water, the liquid products from hydrothermal process and aqueous phase from separation part were analyzed with an HPLC system. The HPLC (Shimadzu, Japan) system composed of a Bio-Rad Organic Acid column Aminex HPX-87H, a refractive index and UV-Vis detectors (210 nm). The mobile phase consisted of aqueous sulfuric acid (5 mM) in water which was set at a flow rate of 0.6 cm^3/min. The column was

operated at 45 °C. The analysis for a sample was completed in 60 min. Each component in the sample was identified by comparing with the retention time of those pure compounds. And the concentrations of each component in the sample were analyzed using calibration curves achieved form standard solution with exactly know concentration.

3.3.3 Determined concentration products sample with GC-FID/ GC-MS

The product samples were analyzed on a GC (Agilent 6890 gas chromatograph) equipped with a DB-WAX Plus column (30 mm × 0.53 mm, DF = 1.00 μm) and a flame ionization detector (FID). The carrier gas was nitrogen with a flow rate of 1.5 ml/min. The hydrogen and air were used for the detector function. The temperature program that used in the analysis is following : initial temperature of 50 °C, kept for 3 min, then warmed to 210 °C with a heating ramp of 80 °C·min−1and kept for additional 2.5 min. The concentration of products sample were determined using calibration curves obtained by analyzing its standard solution with known amount.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Production of levulinic acid from wastewater

4.1.1 Identification of wastewater

Firstly, the acidity of wastewater from nano-crystalline starch production process was investigated with titration techniques. It was found that H_2SO_4 concentration was constant at 2.87 M in each batch of waste water. The organic composition of the waste water from nano-crystalline starch production process was analyzed by HPLC equipped with an Aminex HPX-87X column. The Aminex HPX-87X column is the conventional column for the analysis of carbohydrates in solution with carboxylic acids, volatile fatty acids, short-chain fatty acids, alcohols, ketones, and neutral metabolites. The chromatogram from HPLC technique indicated that only glucose is the main component of wastewater from the nano-crystalline starch production process. The glucose concentration in wastewater varies between 48.30 to 65.20 g/L. It is noted that the polysaccharide content in wastewater was also examined with hydrolysis and HPLC technique. The results from chromatogram showed that the content of glucose did not significantly increase after hydrolysis. Therefore, it can be concluded that no polysaccharide contained in wastewater from nano-crystalline starch production process.

It is noted that the effect of operating parameters (i.e. reaction temperature, and time) on levulinic acid yield production was primary studied over the simulated wastewater with known glucose concentrations. Then, the optimizing conditions that obtain the highest levulinic acid yield were later applied with the real wastewater from nano-crystalline starch production process.

4.1.2 Effect of reaction temperature

To determine the effect of reaction temperature on the conversion of glucose and yield of levulinic acid, the hydrothermal experiments were conducted at 120 - 200 ºC for 240 minutes. The chemical composition of the product sample obtained from the hydrothermal process was analyzed by HPLC (Figure 4.1), from which the chromatogram consists of glucose (RT=9.2 min), formic acid (RT=13.9 min), levulinic acid (RT=16.3 min), and HMF (RT=32.8 min).

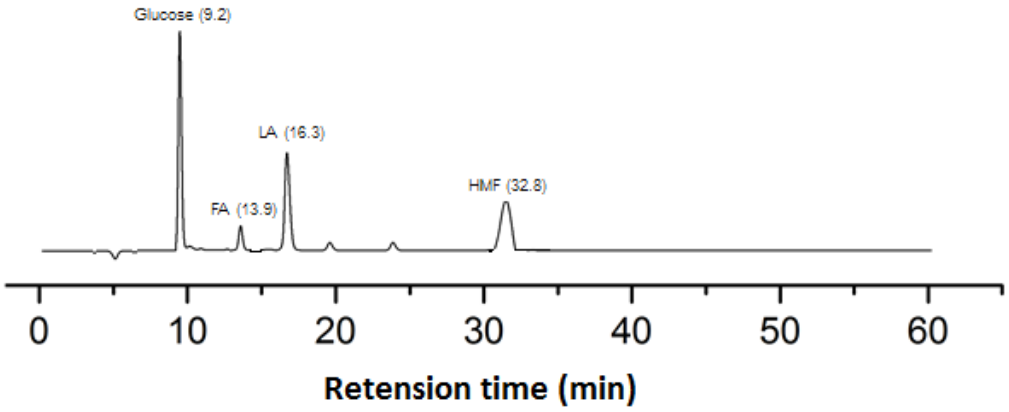


Figure 4.1 Typicall HPLC chromatogram of product sample after hydrothermal process

The influence of temperature on the yield of levulinic acid and the conversion of glucose is shown in Figure 4.2. It indicates that the glucose conversion increases with rising of the reaction temperature (up to 100% conversion at 160ºC), whilst the selectivity or yield of levulinic acid decreased with raising the reaction temperature from 140-220ºC. Furthermore, the amount of humin formation increases with the raising of reaction temperature as shown in figure 4.3(a). Analogously, Chang et al.[15] reported that the activation energy for the HMF formation is 86.33 kJ.mol^{-1}, levulinic acid formation is 56.95 kJ.mol^{-1} and humin formation is 209.5 kJ.mol^{-1}. This report is evident that higher reaction temperature results in a lower yield of levulinic acid because higher temperature resulting in higher energy to formed humin. The composition of carbon and hydrogen in humin for simulated wastewater at various reaction temperature (the data obtained from a CHN analyzer) was showed in table 4.1. The composition of carbon in humin trended to increase with raising reaction temperature, while the composition of hydrogen trend to constant with increasing reaction temperature.

It is noted that at reaction temperature of 120°C, the glucose conversion and levulinic acid formation was dramatically dropped because the energy was not sufficient for completely converting glucose to levulinic acid under these operating conditions (at 120°C and 240 minutes). According to previous study, Tarabanko et al.[13] reported the similar phenomena that the yield and reaction rate of levulinic acid formation increased with the rising reaction temperature at moderate temperature.

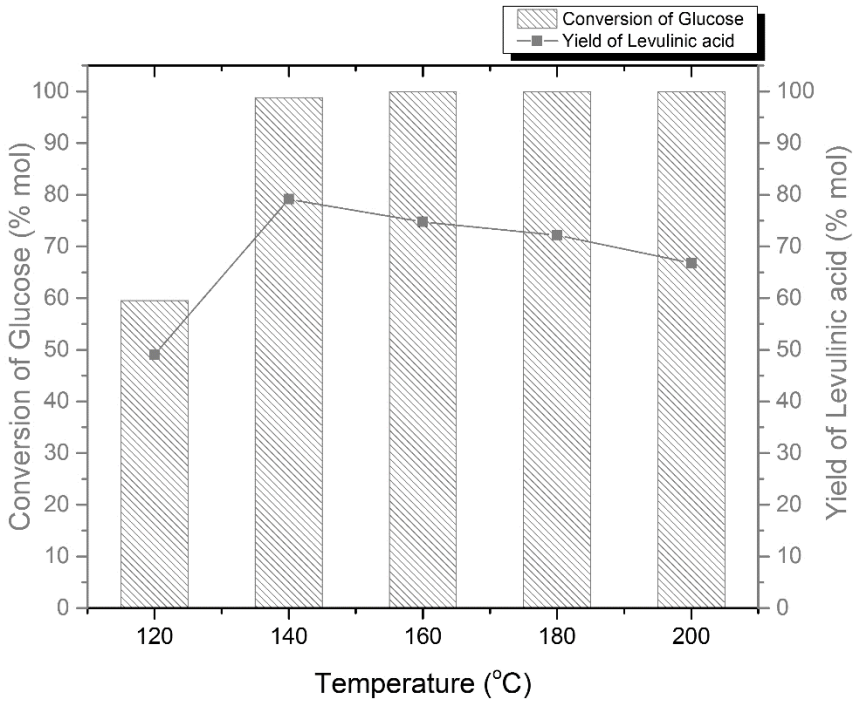


Figure 4.2 Influence of reaction temperature on conversion of glucose and yield of levulinic acid. (Glucose = 45 g/L and Reaction time = 4 hours)

It was also found that humin was generated as a by-product at every reaction temperature that was studied, but HMF and formic acid were not found for every reaction temperatures studied. Girisuta et al.[14] reported that the maximum concentration of HMF in each reaction is usually less than 5% of the glucose concentration and Chang el al.[54] also reported that the formation rate constant of levulinic acid from HMF dramatically increases with raising acid content from 3% to 5%. Therefore, this surveillance indicates that the conversion of glucose to HMF much slower than the conversion of HMF to levulinic acid. For the absent of formic acid

in this experimental, the previous study was reported [83-85] that formic acid is easily decomposed to carbon monoxide and hydrogen in the present of metal or acid catalyst at moderate temperature.

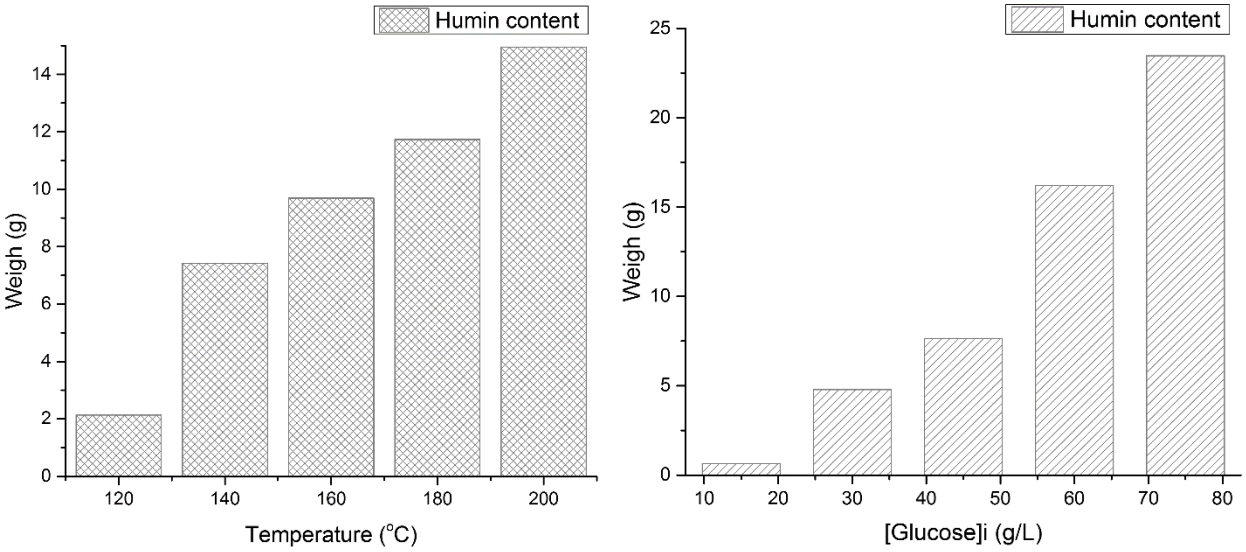


Figure 4.3 Influence of temperature reaction temperature (a) and initial concentration of glucose (b) on humin content for simulated wastewater.

Table 4.1 The composition of carbon and hydrogen in humin for simulated wastewater at various temperatures

Temperature (°C)	Carbon %	Hydrogen %
120	50.80	4.85
140	53.44	4.81
160	53.68	4.64
180	54.78	4.80
200	54.00	4.88

4.1.3 Effect of glucose concentration

The effect of glucose concentration on the production of levulinic acid was conducted by varying the concentration of glucose between 15, 30, 45, 60 and 75 g/L, respectively at 140 ºC for 240 minutes. Figure 4.4 shows the influence of glucose concentration on the yield of levulinic acid and the conversion of glucose. It can be seen that raising the amount of glucose in the range of 15-45 g/L slightly decreases levulinic acid yield and glucose conversion. Both conversion and yield of levulinic acid sharply drops when increasing amount of glucose to 60 and 75 g/L.

4.1.4 Effect of reaction time

The conversion of glucose and yield of levulinic acid from simulated wastewater at several reaction times was then studied. The experiments were conducted at the temperature of 140 °C. The initial concentration of glucose was kept constant at 45 g/L. As shown in Figure 4.5, the conversion of glucose and the yield of levulinic acid dramatically increased from 55.97 and 43.29 % mole at 2 hours of reaction time to 98.77 and 79.15 % mole at 4 hours of reaction time, respectively. For longer reaction times, the conversion of glucose and the yield of levulinic acid slightly increased when reaction time increased from 4 hours to 6 hours (100% and 80.30%, respectively). Therefore, considering in terms of economy and value, the 4 hours reaction time was selected to apply with wastewater for levulinic acid production. Additionally, Jing et al.[16] reported that levulinic acid was stable at 220 ºC in high temperature liquid water. Levulinic acid was only decomposed 1.00% at 220 ºC for 8 hours.

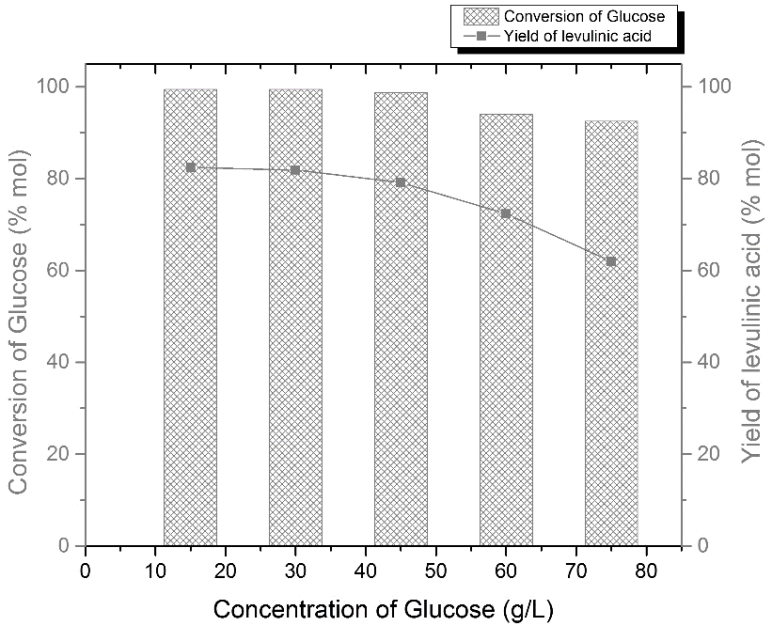


Figure 4.4 Influence of initial glucose on conversion of glucose and yield of levulinic acid. (Glucose = 45 g/L and reaction time = 4 hours)

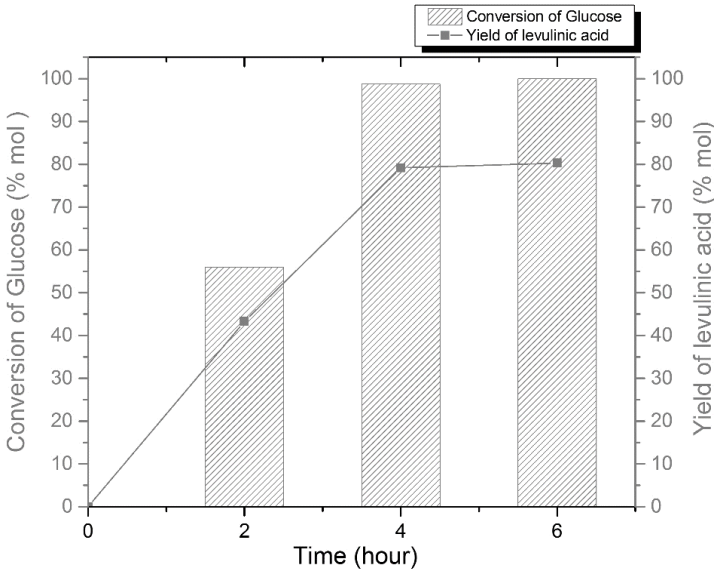


Figure 4.5 Influence of reaction time on conversion of glucose and yield of levulinic acid. (Glucose = 45 g/L and reaction temperature = 140 ^{o}C)

4.1.5 Production of levulinic acid from wastewater

As the next step, the hydrothermal process of real wastewater was carried out at various temperatures (120-220^{o}C) for 240 minutes. The yield of levulinic acid and the conversion of glucose are shown in Figure 4.6. The result indicates that the glucose conversion increases with rising of the reaction temperature (up to 100% conversion at 160^{o}C), whilst the selectivity or yield of levuinic acid decreased with raising the reaction temperature from 140-220^{o}C. This observation indicated that glucose conversion and yield of levulinic acid from the wastewater are in the same trend as those of the simulated wastewater. The maximum yield for levulinic acid production from wastewater was 81.51 % mol in 4 hours at 140 °C of reaction temperature.

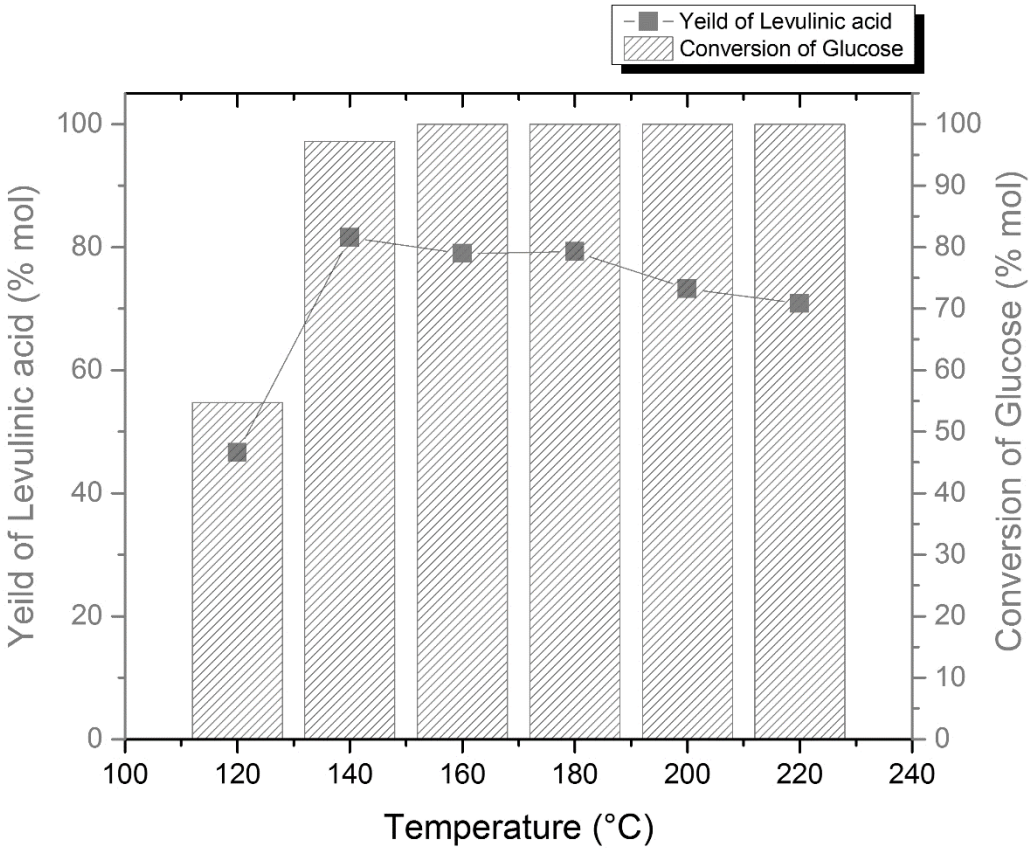


Figure 4.6 Influence of reaction temperature on conversion of wastewater and yield of levulinic acid (Reaction time = 4 hours)

4.2 Separation of levulinic acid from other compounds

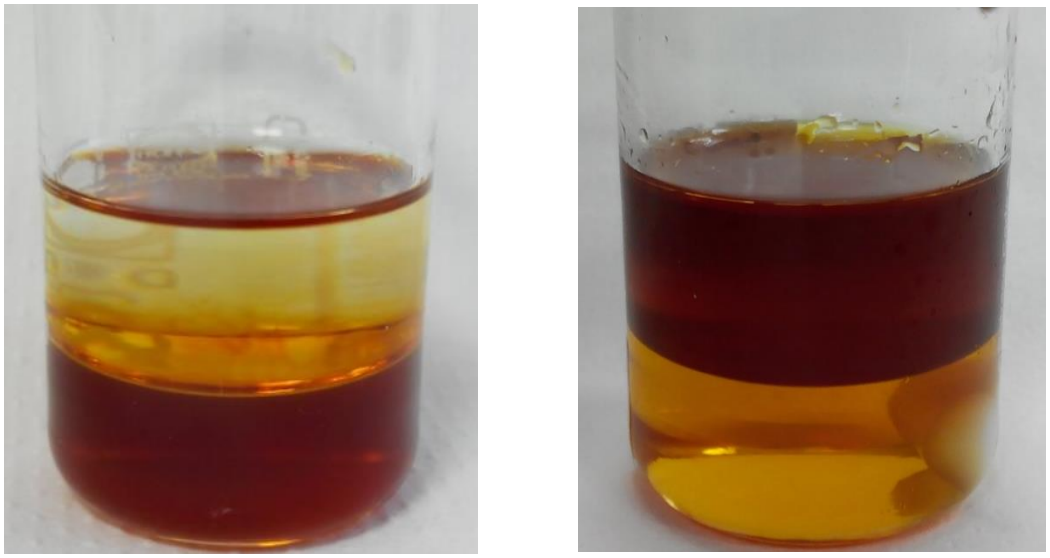
The main drawback for the production of levulinic acid from wastewater is the separation process. The final product from hydrothermal of wastewater is mainly composed of levulinic acid, H_2SO_4 and water. The conventional distillation method is not suitables for separating levulinic acid from H_2SO_4 since H_2SO_4 can cause high corrosive problem to the system. In this study, extraction and reactive extraction were conducted to perform for separation of levulinic acid from products samples. The product samples used as reactants in the separation part obtained from hydrothermal of wastewater at reaction temperature of 140 °C for 4 hours of reaction time. The product samples were firstly extracted humin out, therefore, the mainly composition of product samples were 0.25 M of levulinic acid and 2.87 M of H_2SO_4.

4.2.1 Extraction of levulinic acid

The liquid-liquid extraction of levulinic acid in the aqueous mixtures containing the high acid concentration was performed with Methyl isobutyl ketone and 2-sec-butylphenol at 25 °C and various extraction times (1, 2 and 3 hours). For the extraction of levulinic acid by Methyl isobutyl ketone, a previous study, Dunlop and Wells [86] reported the monitoring of Methyl isobutyl ketone as a water-immiscible solvent for extraction of levulinic acid from the aqueous mixture containing the diluted acid catalyst (H_2SO_4) and levulinic acid. But, different results were obtained at higher acid concentration (H_2SO_4). In my work, when mixed methyl isobutyl ketone with in the aqueous mixtures containing the high acid concentration, the methyl isobutyl ketone was dissolved in aqueous phase. This examination indicated that the methyl isobutyl ketone acted as water-miscible in high acid concentration and unsuitable for separated levulinic acid from the aqueous mixtures containing the high acid concentration. Many previous studies [33, 34, 56] reported that the employed Methyl isobutyl ketone as anion complex for extracted ions H^+ or other cations and Avila Rodríguez et al.[87] also described that the ability to dissolve of Methyl isobutyl ketone in aqueous phase increased with raising the concentration H_2SO_4.

For the extraction of levulinic acid by 2-sec-butylphenol, it was added to the aqueous mixtures containing the high acid concentration in ratio 1:1. The solutions (aqueous phase/organic phase) were stirred with a magnetic stirrer on the hot plate at 150 rpm at 25°C for 1, 2 and 3 hours. Figure 4.7(a) shows the color of organic and aqueous phase before stirred. Firstly, the 2-sec-butylphenol in organic phase is colorless liquid. The color of the 2-sec-

butylphenol in organic phase was changed to brown when levulinic acid dissolved from aqueous phase to organic phase and the color of aqueous phase was changed to light yellow as shown in figure 4.7(b). The concentration of levulinic acid in aqueous phase was determined with HPLC system. In the aqueous phase, the concentration of levulinic was reduced to 0.125, 0.075 and 0.075 M for the extraction times 1, 2 and 3 hours, respectively. Then the extraction time of 2 hours is enough time to reach equilibrium. The highest extraction efficiency of levulinic acid from the aqueous mixtures containing the high acid concentration (H_2SO_4) by using 2-sec-butylphenol as extractant at 25 ° C was obtained value of 70.0 mol %.



(a) (b)

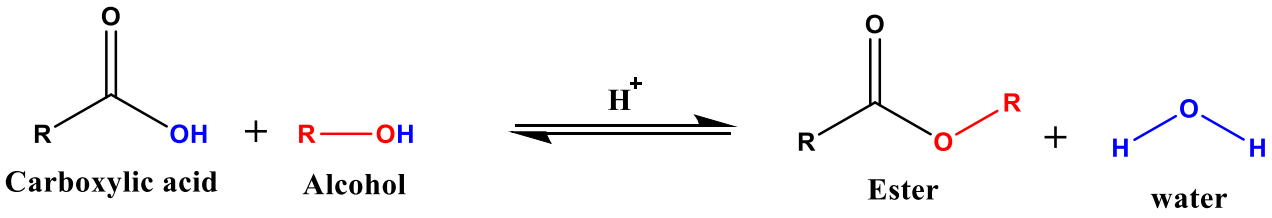
Figure 4.7 The mixture solution (organic phase/aqueous phase) (a) before and (b) after stirred 300 rpm with magnetic stirrer at 25 °C for 3 hours.

Analogously, Alonso et al. [84] described the advantage of using alkyl phenol solvent for selectively extract of levulinic acid from mixture aqueous solutions of sulfuric acid. Firstly, the H_2SO_4 was not appeared in organic phase for all experimental. Secondly, the alkyl phenol has flexibility for modified the hydrophobicity of the molecule. The solubility of the alkyl phenol in aqueous phase increases with the present of shorter alky chain. On the other hand, the boiling point of alkyl phenol increases with the present of longer alky chain. The sufficient

length of alkyl chain have higher boiling points than does levulinic acid which means that levulinic acid was distillated at top of a distillation column instead the evaporation of solvent as normally method.

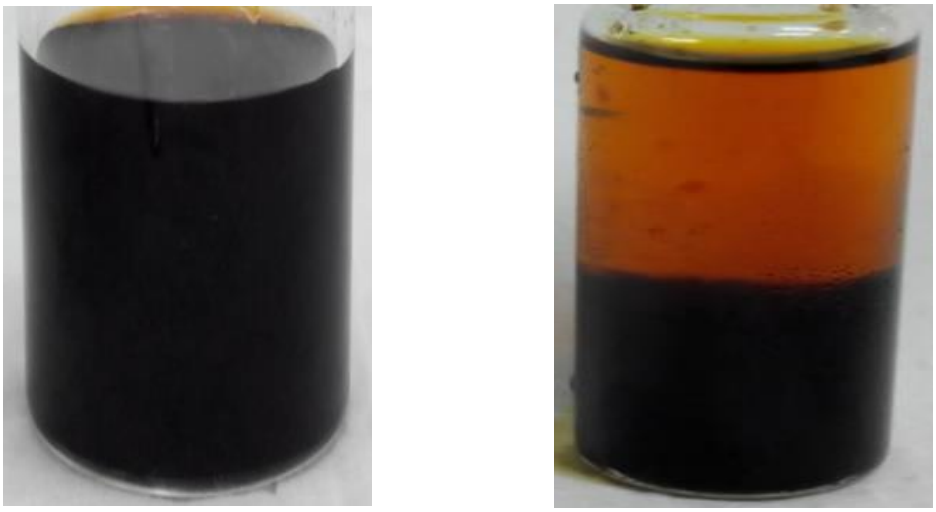
4.2.2 Reactive extraction of levulinic acid

The reactive extraction of levulinic acid in the aqueous mixtures containing the high acid (H_2SO_4) concentration and levulinic acid was demonstrated with various types of alcohol (2-propanol, butanol and 2-butanol). Typically, the reactive extraction of carboxylic acid from aqueous phase with alcohol at present of acid catalyst was obtained hydrophobic ester. And the hydrophobic ester was spontaneously separated from the aqueous phase. The aqueous mixtures contain high acid concentration and levulinic acid was miscible mixed with all type of alcohol in this experimental. The ratio of a mixture between aqueous containing the high acid concentration and alcohol is equal to 10:30 by volume. In this study, H_2SO_4 in aqueous mixtures acted as homogenous acid catalyst. The reaction was carried out in pressure reactor at various reaction temperature (80, 100, 120 °C) for 2 hours. The results from HPLC chromatogram indicated that the aqueous mixtures containing 0.25 M of levulinic acid and 2.87 M of H_2SO_4 was not reacted with all type of alcohol (2-propanol, butanol and 2-butanol) due to natural of esterification reaction. The esterification reaction is reversible reaction as shown in scheme 4.1. When the esterification reaction containing the high amount of water, the esterification reaction reverses to carboxylic acid and alcohol. Therefore, the removal of water by an evaporation step for obtaining a more concentrated solution of levulinic acid and sulfuric acid before the reactive extraction of levulinic acid with alcohol was required.



Scheme 4.1 Esterification of carboxylic acid with alcohol in the presence of an acid catalyst

The aqueous mixtures containing the high acid concentration and levulinic acid was evaporated at 60 °C for 3 hours under pressure of 0.010 bars. The concentration after achieved evaporation step of levulinic acid was determined with HPLC system. For the concentration after achieved evaporation step of H_2SO_4 was checked with titration method. The concentration of levulinic acid and H_2SO_4 after achieving evaporation step increased to 1.85 M and 12.59 M, respectively.



(a) **(b)**

Figure 4.8 Mixtures of solution of concentrated aqueous solution (containing the H_2SO_4 and Levulinic acid) and 2-butanol (a) before and (b) after reacting in pressure reactor at reaction temperature of 100 °C for 2 hours.

For the reactive extraction of concentrated aqueous solution (containing the H_2SO_4 and levulinic acid) with various type of alcohol (2-propanol, butanol and 2-butanol) at various reaction temperature (80, 100, 120 °C) for 2 hours, only 2-butanol was achieved reactive extraction with concentrated aqueous solution (containing the H_2SO_4 and levulinic acid). The concentrated aqueous solution (containing the H_2SO_4 and levulinic acid) was reacted with 2-butanol to obtain 2-buthyl levulinate ester. The product sample was confirmed with gas chromatography-mass spectrometry, as shown in Figure 4.9. The concentration of 2-buthyl

levulinate ester was determined with gas chromatography by using GVL as internal standard. The conversion of levulinic acid at various reaction temperatures (80, 100, 120 °C) are 83.53, 87.04 and 84.42 mol%, respectively. The yields of 2-buthyl levulinate ester are 72.43, 75.03, and 70.23 mol %, respectively. The other type of alcohol (2-propanol, butanol) were esterified with concentrated aqueous solution (containing the H_2SO_4 and levulinic acid) to obtained 2-proply levulinate ester and buthyl levulinate ester, but there were not separated spontaneously from the aqueous phase. In consequence, the alkyl group in 2-proply levulinate ester and buthyl levulinate ester was not enough hydrophobicity for spontaneously separated from the aqueous phase.

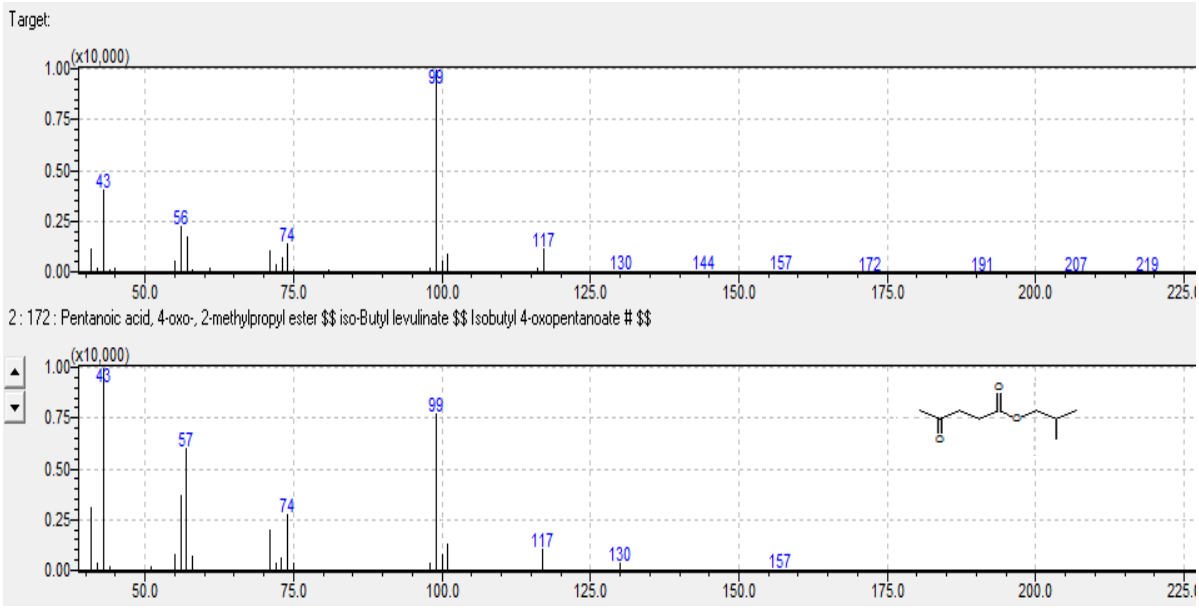


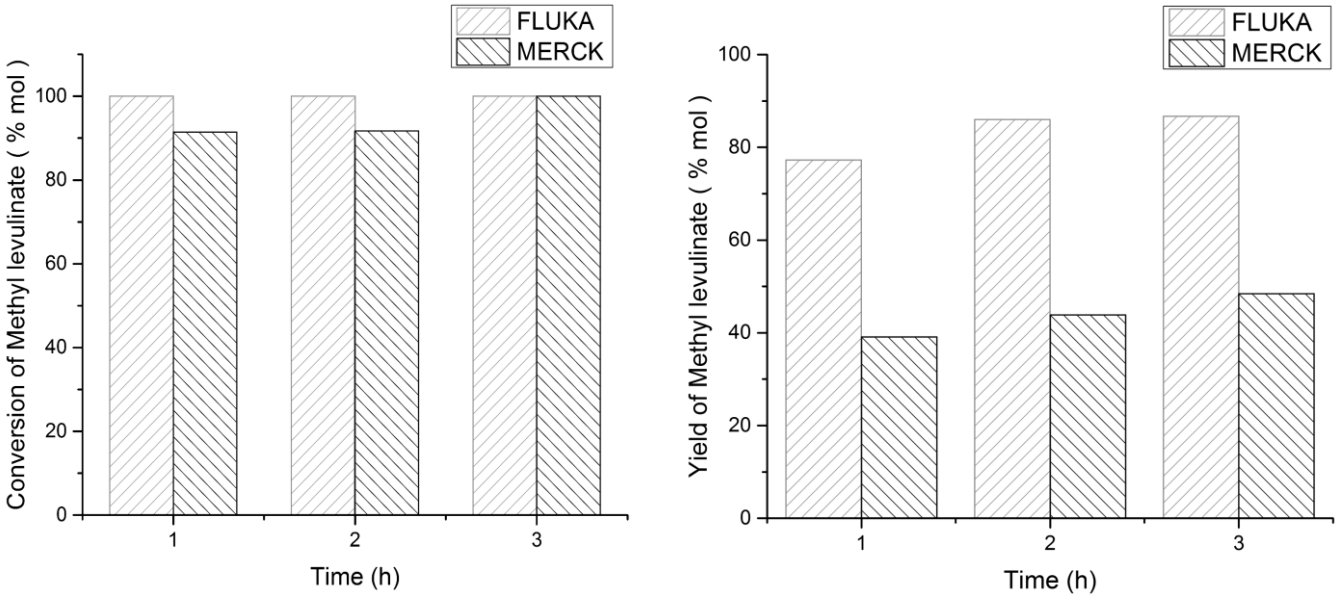
Figure 4.9 Mass spectrum of product sample compared with 2-buthyl levulinate ester.

4.3 Production of γ-valerolactone (GVL) from alkyl levulinate ester

In this work, levulinic acid was then employed as a precursor for the production of γ-valerolactone (GVL). This compound is considered to be one of the most attractive molecules. γ-valerolactone has the feasibility to be used as a solvent, liquid fuel ,fuel additive and precurser for novel polymers or alkanes [76, 88-92]. Typically, γ-valerolactone was produced from hydrogenation of Levulinic acid or levulinate ester by uging metal catalyst (such Au, Rh, Pt, Pd, Ru, Re) in the present of hydrogen at high pressure and temperature. This part intended to study the possibility for the production of γ-valerolactone from akyl levulinate ester (methyl levulinate and ehtyl levulinate) via catalytic tranfer hydrogenation, which reacted at lower temperature and not required high pressure of hydrogen, by using Raney as catalyst and 2-proparnol as hydrogen donor.

4.3.1 Influence of RANEY® brand on the production of γ-valerolactone

The conversion of methyl levulinate and yield of γ-valerolactone from different brands of RANEY catalyst (Fluka and Merck) at various reaction times was studied. The amounts of methyl levulinate, 2-propanol and RANEY were kept constant at 2.32 mmol, 12.0 ml and 0.50 g, respectively. The experiments were conducted at the temperature of 100 °C in reflux system. It was found that alkyl γ-hydroxypentanoates as by-product were observed at every reaction studied. The conversion of methyl levulinate that using RANEY form Fluka as catalyst was reached 100 % mol at 1 hour of reaction temperature, while the conversion of methyl levulinate that using RANEY form Merck as catalyst was increasing with reaction time to reaching 100 % at 3 hours as show in figure 4.10(a). h using RANEY form Fluka and Merck as catalyst was about 77.28 and 39.40 % mol (Figure 4.10(b)), respectively.The yield of γ-valerolactone from both brand of RANEY was slightly increased with raising reaction time. The different between yields of γ-valerolactone from the reaction that using RANEY form Fluka and Merck as catalyst was explained by surface area. The physical properties of RANEY form Fluka and Merck were determined with BET. It indicated surface area of RANEY form Fluka and Merck were 58.48 and 34.73 m^2/g, respectively. Then, the RANEY from Fluka was chosen for the next experimental studies.



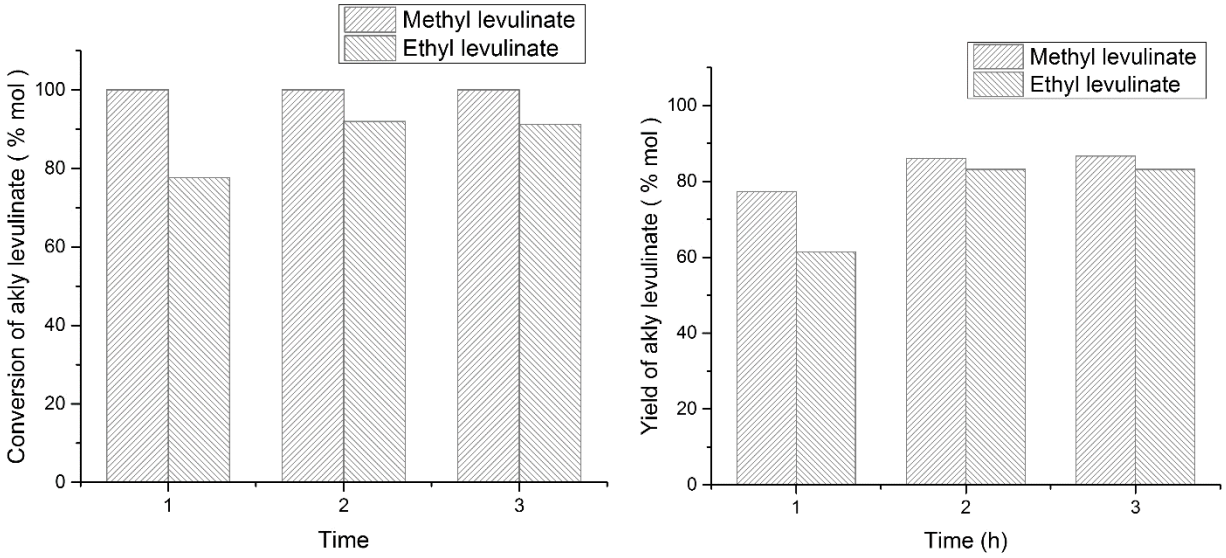
(a) (b)

Figure 4.10 Influence of RANEY®'s brand (Fluka and Merck) on conversion of (a) levulinate ester and (b) yield of γ-valerolactone at reaction temperature of 100 °C in reflux system (Air atmosphere).

4.3.2 Influence of akly group on γ-valerolactone production

The effect of an alkyl group in levulinate ester on the production of γ-valerolactone via the catalytic transfer hydrogenation process was investigated. The experiments were conducted with various type of levulinate ester (methyl levulinate and ethyl levulinate) at reaction temperature of 100 °C in the presence of RANEY from Fluka for 3 hours of reaction time. Figure 4.11 shows influence of alkyl group in levulinate ester on conversion of levulinate ester and yield of γ-valerolactone. The conversion of methyl levulinate was increased to 100 % mol at 1 hour of reaction temperature, while the conversion of ethyl levulinate at 1 hour of reaction temperature was 77.64 % mol which increased with reaction time. The yield of γ-valerolactone was also the same trend as with conversion. The yield of γ-valerolactone from both methyl levulinate and ethyl levulinate were raised with the increasing of reaction time. The yield of γ-

valerolactone from methyl levulinate was higher than the yield of γ-valerolactone from ethyl levulinate in all range of reaction time due to steric effect in the longer chain of alkyl group in levulinate ester. Therefore, methyl levulinate was chosen as reactant for the next experimental studies.



(a) (b)

Figure 4.11 Influence of alkyl group in levulinate ester on (a) conversion of levulinate ester and yield of (b) γ-valerolactone at reaction temperature of 100 °C in the presence of RANEY from Fluka (reflux system).

4.3.3 Influence of reaction tempreature on γ-valerolactone production

The effect of reaction temperature on the conversion of methyl levulinate and yield of γ-valerolactone was further investigated. The catalytic transfer hydrogenation process of methyl levulinate was carried out with 2-propanol in the present of RANEY from Fluka at various temperatures (40-100 °C) for 3 hours of reaction time. The results are shown in Figure 4.12. The conversion of methyl levulinate and yield of γ-valerolactone increased with the raising reaction temperature. The highest conversion of methyl levulinate and yield of γ-valerolactone

was 100 and 86.70 mol %, respectively. In addition, the yield of alkyl γ-hydroxypentanoates increased with decreasing of reaction temperature.

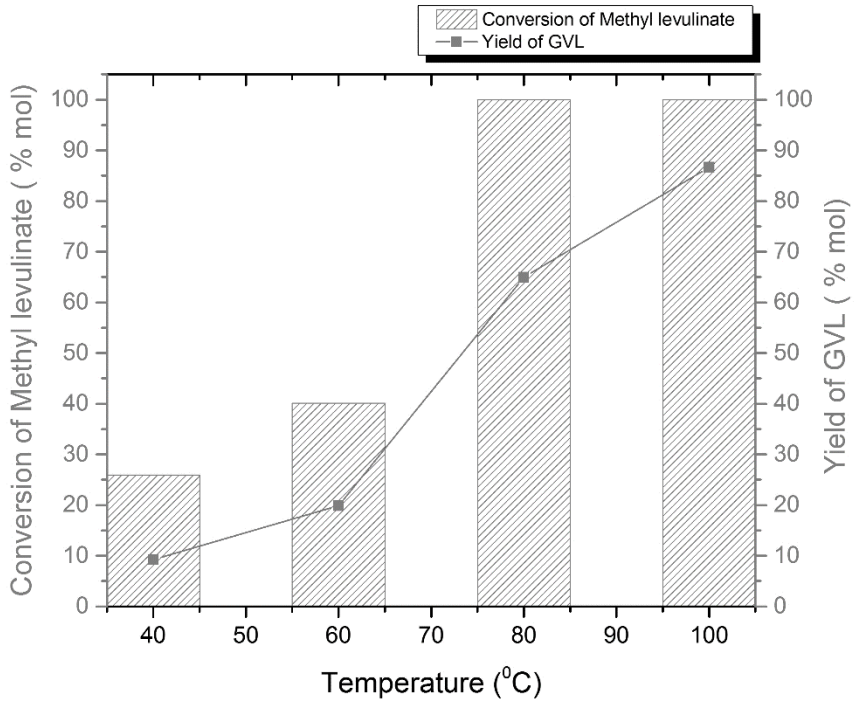


Figure 4.12 Influence of reaction temperature on the conversion of methyl levulinate and yield of γ-valerolactone in the presence of RANEY from Fluka at 3 hours of reaction time. (Reflux system).

4.3.4 Influence of reactor type on γ-valerolactone production

The influence of reactor type on the conversion of methyl levulinate and the yield of γ-valerolactone were examined. The catalytic transfer hydrogenation reaction of methyl levulinate by using 2-propanol as hydrogen donor was performed in either a reflux system or a pressure reactor at reaction temperature of 100 °C in the presence of RANEY from Fluka. Figure 4.13 shows the influence of reactor type on production of γ-valerolactone form methyl levulinate. The conversion of methyl levulinate in reflux system was reached 100 mol % at 1 hour of reaction temperature, while the conversion of methyl levulinate in pressure reactor was reached 100% mol at 2 hours of reaction temperature. For the γ-valerolactone, at first 2 hours the yield

of γ-valerolactone in reflux system is higher than yield of γ-valerolactone in pressure reactor. The yields of γ-valerolactone in both systems trended to increase with raising reaction time from 1 to 3 hours. However, the yield of γ-valerolactone in reflux system trended to constant about 86 mol %, which could be due to the nature of each system and the boiling point of 2-propanol as hydrogen donor in reaction.

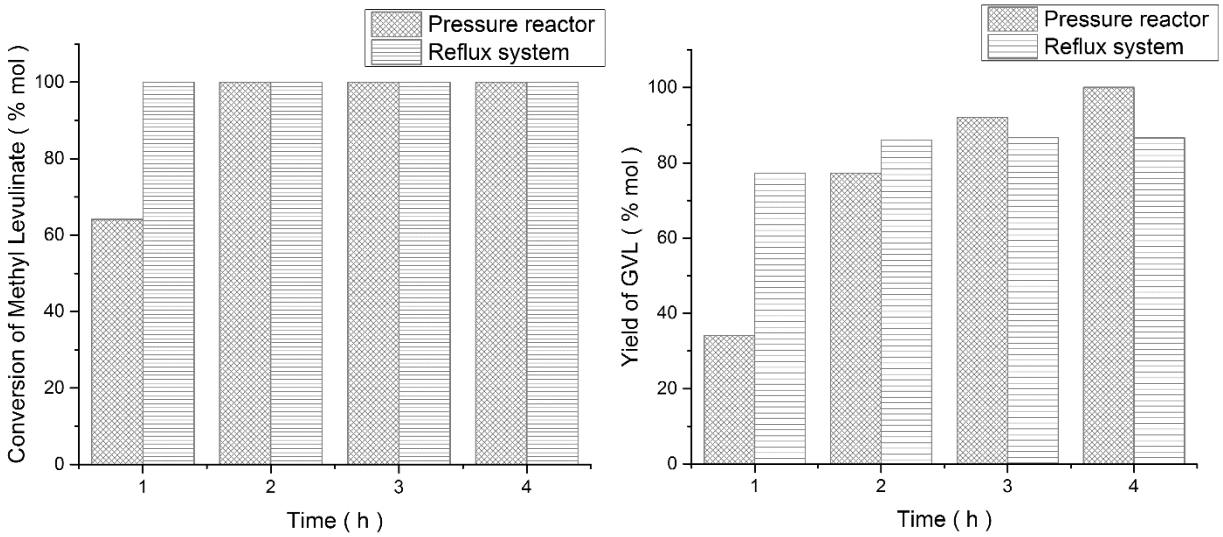


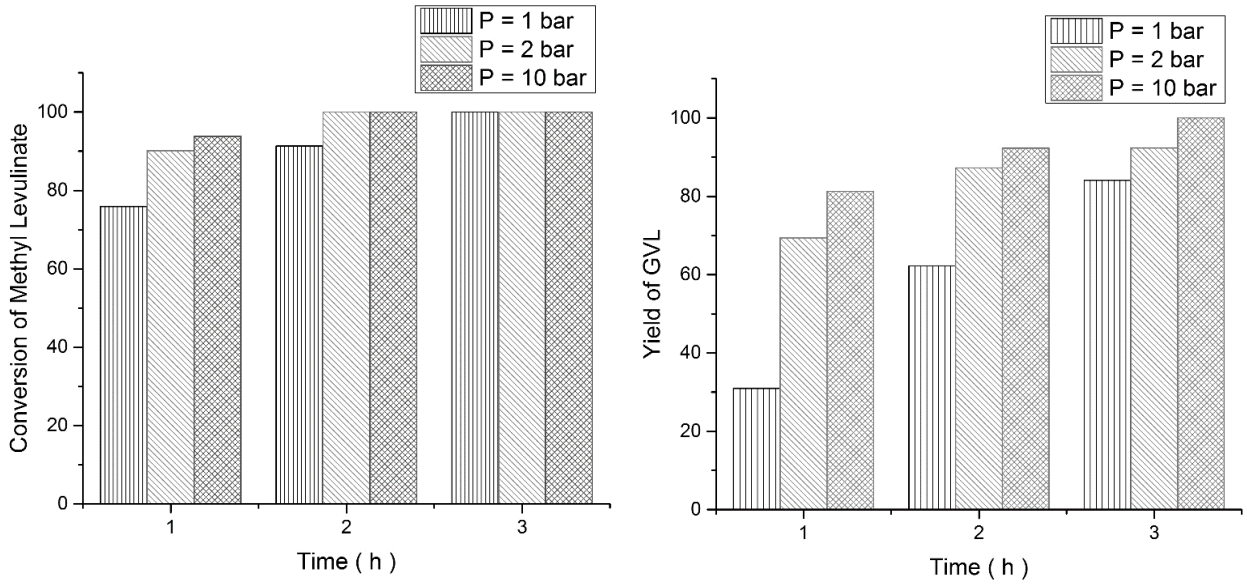
Figure 4.13 Influence of system on (a) the conversion of methyl levulinate and (b) yield of γ-valerolactone at reaction temperature of 100 °C in the presence of RANEY from Fluka.

A reflux reactor system is the isobaric process that maintains the pressure at atmospheric pressure through the operating time by condensing the reactant from vapor phase to liquid phase (reactant consumes a lot of energy to vaporize and built up the temperature system sunk by the cold liquid reactant from the condensing unit). On the other hand, a pressure reactor system is the isochoric process, i.e. the pressure inside the pressure reactor increases with rising of reactant vapor which convert from the liquid phase. Note that, to reach the temperature set point at the similar time, the reflux reactor system has to spend the energy to the system more than the energy using of the pressure reactor system.

Considering the characteristic of the reflux reactor system for catalytic transfer hydrogenation reaction at 100 °C, 2-propanol was vaporized (2-propanol consumed energy to change from liquid phase to vapor phase) and condensed by transfers energy to condenser which contained cooling water at 9 °C. As describe above paragraph, at the same heating rate, this characteristic indicated that the energy for stabilize temperature to 100 °C in a reflux reactor system was used more than the reaction in a paressure reactor system. Therefore the conversion of methyl levulinate and yield of γ-valerolactone, at the initial state (reaction time of 1 h), in reflux reactor system is higher than yield of γ-valerolactone in pressure reactor system. However, after 2 h, the yield of γ-valerolactone in reflux system was trended to constant whilst, in the pressure reactor process, the yield of γ-valerolactone was trended to increase because of raising the pressure system by the reactant vapor and reached 100 % at 4 h. This observation hints the reaction pressure significant influence to yield of γ-valerolactone.

4.3.5 Influence of pressure on the production of γ-valerolactone

The influence of pressure on the conversion of methyl levulinate and yield of γ-valerolactone was studied. The catalytic transfer hydrogenation reaction of methyl levulinate by using 2-propanol as hydrogen donor was performed with various reaction pressure (N_2 at 1, 2 and 10 bar) at reaction temperature of 100 °C in the present of RANEY from Fluka. Figure 4.14 shows the influence of reaction pressure on the conversion of methyl levulinate and yield of γ-valerolactone. It was found that the selectivity and yield of γ-valerolactone tended to increase with the raising of reaction pressure. For this reason due to the fact in the collision theory that the number of collision increasing with raising reaction pressure. In addition, at high reaction pressure resulting to high boiling point of 2-propanol which protected the loss of 2-propanol in to gas phase and loss of energy in system for change 2-propanol in liquid phase to gas phase.



(a) **(b)**

Figure 4.14 Influence of reaction pressure (N_2) on (a) the conversion of methyl levulinate and (b) yield of γ-valerolactone at reaction temperature of 100 °C in the presence of RANEY from Fluka (Pressure reactor).

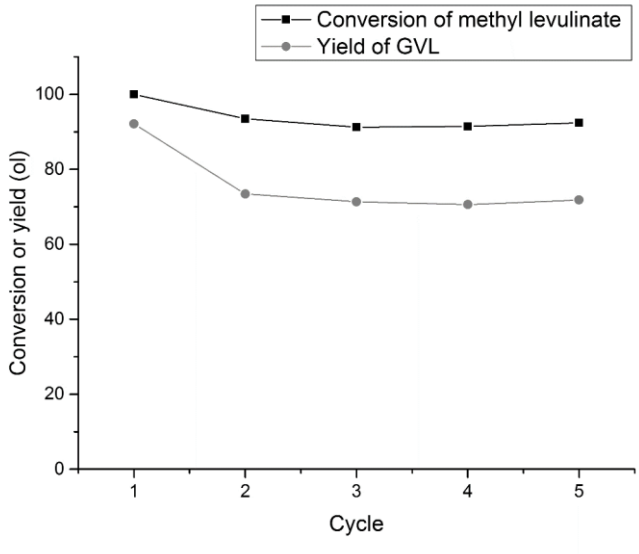


Figure 4.15 Influence of recycling catalyst (RANEY) on the conversion of methyl levulinate and yield of γ-valerolactone at reaction temperature of 100 °C in air atmosphere for 3 hours of reaction time.

4.3.6 Recyclability of RANEY for the production of γ-valerolactone

In this part, the catalytic stability of RANEY from Fluka was appraised by reusing RANEY in the catalytic transfer hydrogenation reaction of methyl levulinate and compared the conversion of methyl levulinate and yield of γ-valerolactone with a fresh catalyst. The condition for the catalytic stability test is 100 °C of reaction temperature in air atmosphere for 3 hours of reaction time. The Raney was reused four times under these conditions. Figure 4.14 showed the influence of a recycling catalyst (RANEY) on the conversion of methyl levulinate and yield of γ-valerolactone. The conversion of methyl levulinate and yield of γ-valerolactone in reclying catalyst relative lower compared with fresh catalyst. And the conversion of methyl levulinate and yield of γ-valerolactone after the second cycle of catalyst was trended to slightly decrease. This reason was due to the prohibitive effect of methanol (obtained from the intramolecular trans esterification of hydroxy levulinic ester). The methanol was absorbed on the surface of the Raney catalyst and then cleaved to an alkoxide group which would block the active site on the Raney catalyst [20, 93, 94]. However, in this study, the ratio of 2-propanol and releasing methanolvis very low then the prohibitive effect of methanol was slightly effected on conversion of methyl levulinate and yield of γ-valerolactone. Analogously, Wang and Rinaldi. [93] reported that the surface of Ni may permanently adsorb by the primary alcohol in the absence of 2-propanol.

CHAPTER 5
CONCLUSION

The wastewater from nano-crystalline starch production process has great feasibility and potential as a resource for the production of levulinic acid because it contains high sugar and acid concentrations.

From the study, it was found that the selectivity and yield of levuinic acid slightly decreased with raising reaction temperature. At low reaction temperature, the reaction required longer time to accomplish the glucose conversion and levulinic acid formation. The optimal conditions of levulinic acid production from waste water were achieved at 140 °C for 240 min, which results in the highest levuinic acid yield of 91.41 % mol. For the liquid-liquid extraction, 2-sec-butylphenol can extracted levulinic acid from the aqueous mixtures containing the high acid concentration. The extraction was reach equilibrium at 2 hours. The highest extraction efficiency is 70.0 mol %. For reactive extraction, 2-butanol was achieved reactive extraction. The conversion of levulinic acid and yield of 2-buthyl levulinate ester is 87.0 % and 75 % by mol, respectively. The akly levulinate ester has high possibility for the production of γ-valerolactone via catalytic transfer hydrogenation by using 2-propanol as hydogen donor in the present of Raney. It was found that the conversion and yield of γ-valerolactone increasing with raising reaction temperature, reaction time and reaction pressure. On the other hand, the conversion and yield of γ-valerolactone reduced with raising akly group in levulinate ester.

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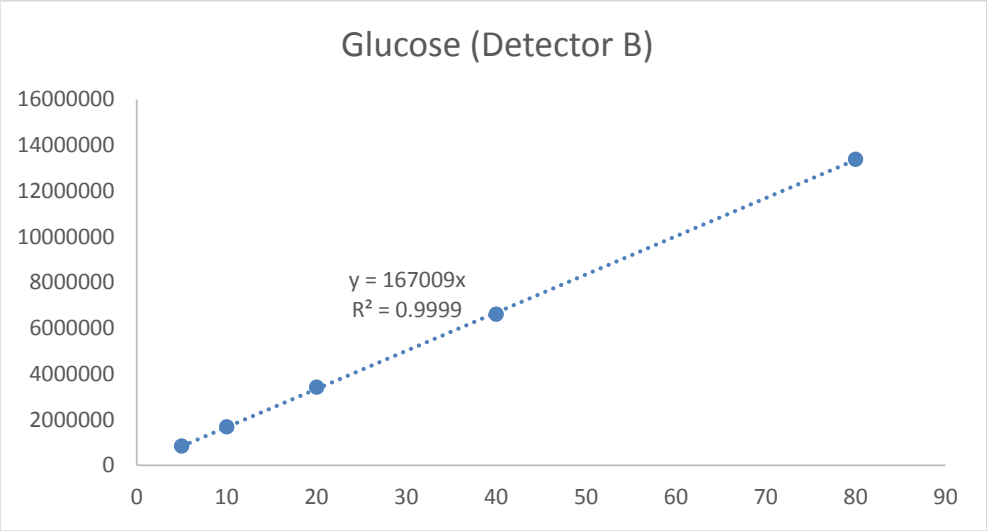
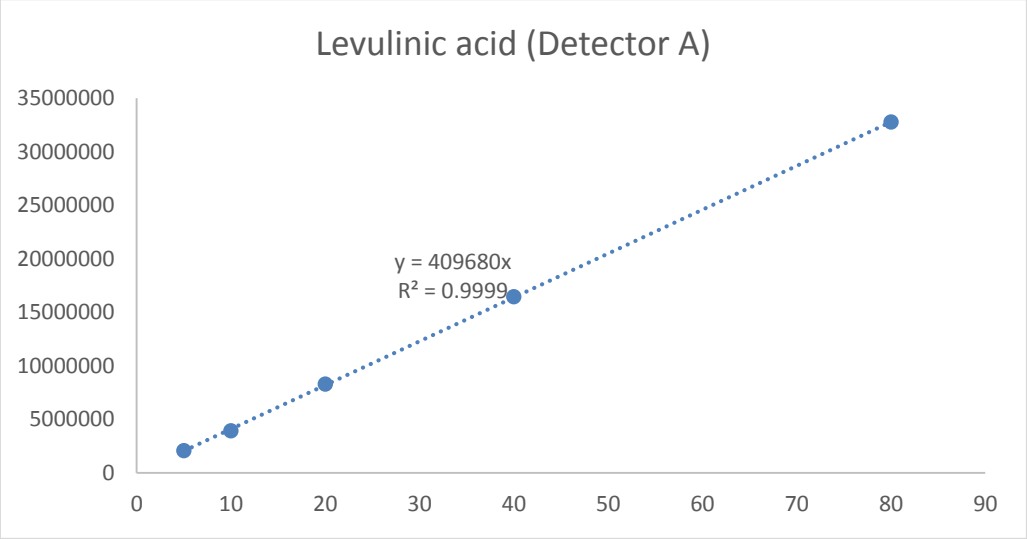
APPENDIXES

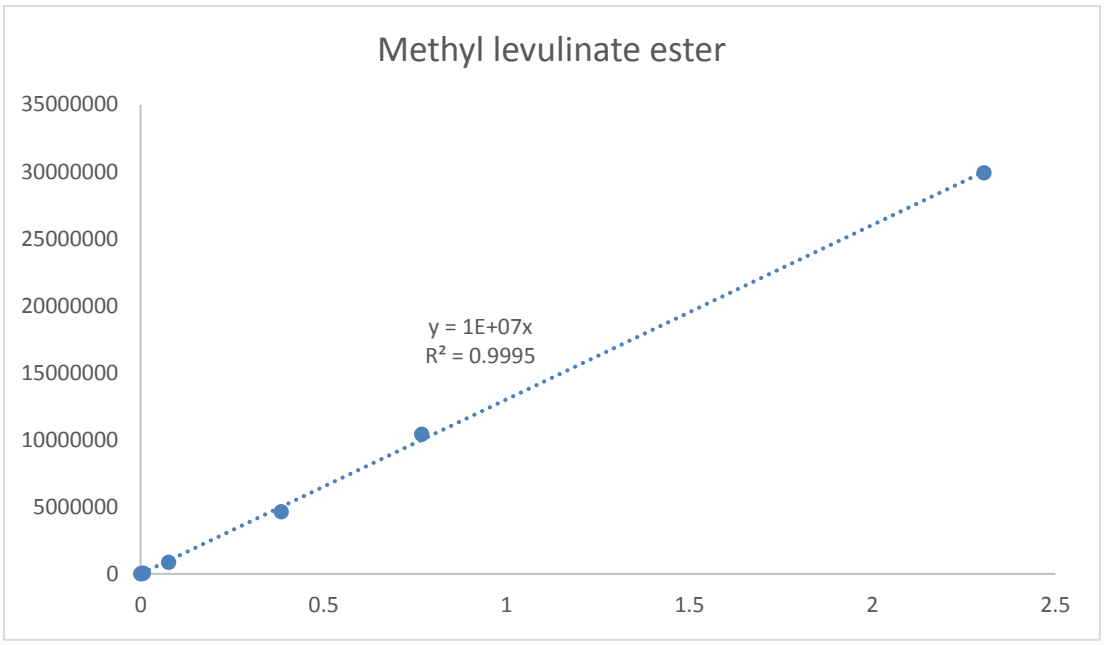
APPENDIXES A: Standard curves



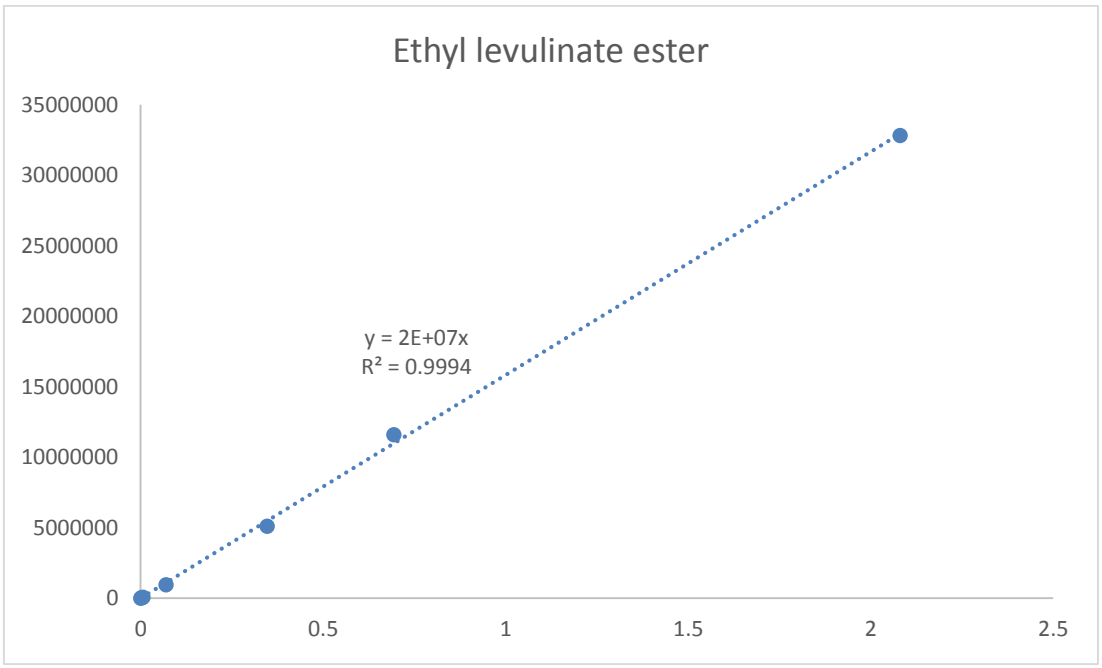
A-1 Standard calibration curve of glucose by RI detector in HPLC



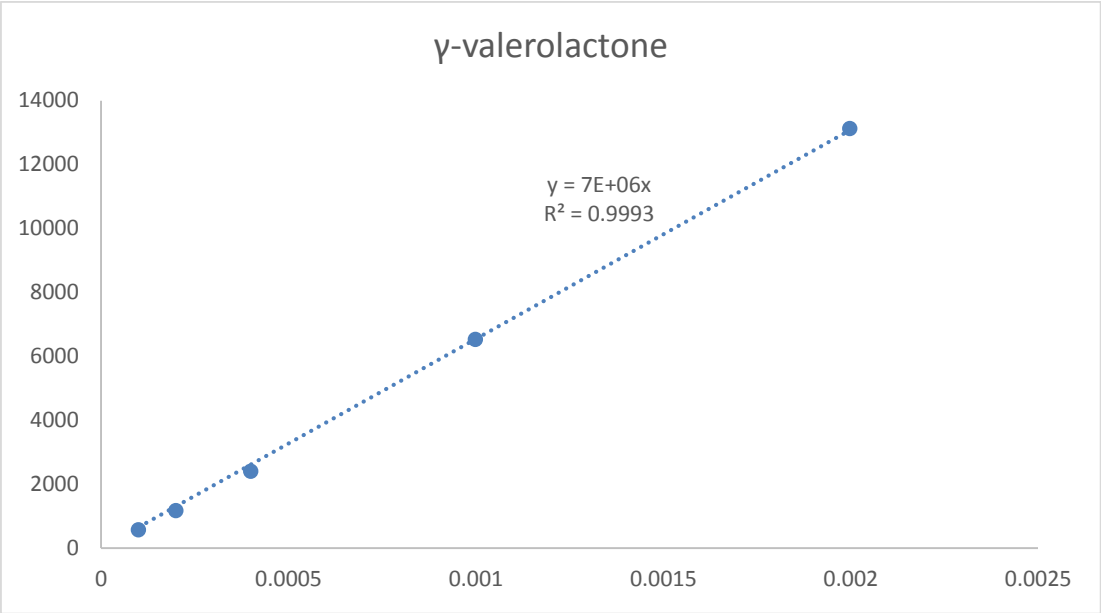
A-2 Standard calibration curve of levulinic acid by UV-Vis detectors (210 nm) in HPLC



A-3 Standard calibration curve of methyl levulinate ester by GC-FID



A-4 Standard calibration curve of ethyl levulinate ester by GC-FID



A-5 Standard calibration curve of γ-valerolactone by GC-FID