Catalytic production of levulinic acid from matured coconut water

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Abstract. Depletion of fossil as fuel resources due to increasing energy demands has led to a challenging transition to renewable abundance bio-based feedstock. Levulinic acid is a versatile platform chemical that can be utilized to produce fuels, solvents, polymers, pharmaceutical and agrochemical products. It can be synthesized from natural resources such as lignocellulosic biomass, sugars and environmental waste. Matured coconut water is an agro waste that produced mainly from coconut milk industry which contains variety of sugars and minerals. This study was carried out on synthesizing levulinic acid from matured coconut water by focusing on the effect of catalytic acid to coconut water ratio, types of acid and reaction time. The matured coconut water was mixed with sulfuric acid at three different concentrations (0.5 M, 0.75 M, 1.0 M) in 9:1, 8:2, and 7:3 ratios respectively. Mixtures were heated at 100˚C for 30 minutes. The ratio decided was carried out into determine the best types of acid (sulfuric acid, hydrochloric acid, phosphoric acid) followed by the reaction time (15, 30, 45, 60 minutes). Levulinic acid production increase as concentration of acid increase. However, low acid percentage in coconut water medium was appropriate enough to give high yield of product (0.135%). Both hydrochloric and sulfuric acid catalyzed more product at high concentration.

1. Introduction
Increasing demand on fossil fuels particularly in petrochemical industry requires new replacement for this resource [1]. Biomass is the only carbon sources that can be used in production of liquid hydrocarbons and chemicals [2]. Levulinic acids has been identified as potential platform chemical in fuel production by the US Department of Energy [5]. It is derived from degradation of sugars or cellulose. Naturally, lignocellulosic biomass consists of three polymers that are cellulose, hemicellulose and lignin that exist in a matrix form to prevent depolymerization and transformation [3]. Acids or enzymes are usually used to degrade the polymer of biomass into formation of simple sugar such as glucose, galactose and xylose.

Waste product from coconut industry such as matured coconut water contains variety of sugars including glucose, fructose and sucrose as it also rich with minerals (table 1) [4]. Under harsh processing conditions, sugar can be converted into useful levulinic acid [3].
Table 1. Composition of coconut water in different stage of maturity [4]

| Physicochemical properties | Stage of maturity coconut (months) |
|----------------------------|-----------------------------------|
|                            | 5-6  | 8-9  | >12 |
| Volume of water (mL)       | 684  | 518  | 332 |
| Total dissolved solid (*Brix) | 5.6  | 6.15 | 4.85 |
| Titratable acidity (%)     | 0.089| 0.076| 0.061|
| pH                         | 4.78 | 5.34 | 5.71 |
| Turbidity                  | 0.031| 0.337| 4.051|

**SUGARS CONTENT**

- Fructose (mg/mL): 39.04, 32.52, 21.48
- Glucose (mg/mL): 35.43, 29.96, 19.06
- Sucrose (mg/mL): 0.85, 6.36, 14.37

**MINERALS**

- Potassium (mg/100mL): 220.94, 274.32, 351.10
- Sodium (mg/100mL): 7.62, 5.60, 36.51
- Magnesium (mg/100mL): 22.03, 20.87, 31.65
- Calcium (mg/100mL): 8.75, 15.19, 23.98
- Iron (mg/100mL): 0.294, 0.308, 0.322
- Protein (mg/mL): 0.041, 0.042, 0.217
- Total phenolic content (mg/mL): 54.00, 24.59, 25.7

Levulinic acid or gamma-ketovaleric acid is a short-chain fatty acid, having a group of ketone carbonyl (CO) and a carboxylic acid (COOH). It is a versatile chemical with a variety of potential usage such as raw material for synthesis of pharmaceutical products, plastic production, polymer resins, textile dyes, animal feed additives, fuel additives, antifreeze and antimicrobial foods [6]. In recent years, the potential of levulinic acid had attracted attention of many researchers [7]. Girisuta has provided a comprehensive study on the various carbohydrate feedstocks used to produce levulinic acid [8]. The production of levulinic acid from carbohydrates involves dehydration of hexose sugars (such as glucose, fructose, sucrose) for hydroxylation of HMF to levulinic acid and formic (Figure 1).

![Figure 1. Acid-catalyzed decomposition of glucose to levulinic acid](image)

The most common catalyst used for producing levulinic acid is mineral acid such as sulfuric acid, hydrochloric acid and phosphoric acid [9]. Even though many heterogeneous catalysts have been used in previous study, problems regarding with separation of catalysts from mixtures is still become a concern [10]. In this study, the potential of matured coconut water as raw material for levulinic acid production was investigated with the help of mineral acids as catalyst.

2. Methodology

2.1 Determination of matured coconut water ratio into acid

The sulfuric acid was diluted into three different concentrations that were 0.5 M, 0.75 M and 1.0 M. For each concentration, the acid was added into matured coconut water by 9:1, 8:2 or 7:3 ratios to make 100
3 ml of mixture. The solution was placed in 500 ml round bottom flask and heated at 100 °C for 30 minutes to measure the amount of levulinic acid produced. The yield was analyzed by High Performance Liquid Chromatography (HPLC).

2.2 Determination of potential acid catalyst
Hydrochloric acid, sulfuric acid and phosphoric acid were diluted into 0.5 M, 0.75 M and 1.0 M concentration. The catalyst was added into matured coconut water to make 100 ml solution according to the best ratio decided from method above. The mixture was placed in 500 ml round bottom flask and heated at 100 °C for 30 minutes to measure the amount of levulinic acid produced. The yield was analyzed by High Performance Liquid Chromatography (HPLC). The best acid catalyst was decided.

2.3 Effects of reaction time on levulinic acid production
The selected acid in three concentrations (0.5, 0.75, 1.0 M) with appropriate ratio was heated in different duration that were 15, 30, 45 and 60 minutes respectively.

2.4 Levulinic acid and formic acid analysis
All samples were filtered to remove the particulate residues and injected into a high performance liquid chromatography (HPLC) system. The analytical column used was an Phenomenex C18 250 mm column. The operating temperature was maintained at 40 °C using 95% of 20 mM sulfuric acid and 5% acetonitrile mobile phase while the volumetric flow rate was maintained at 0.6 ml/min.

2.5 Modelling technique for simulation of levulinic acid production
The kinetic parameters for the proposed kinetic model were estimated using a maximum-likelihood approach, which is based on minimization of errors between the experimental data and the kinetic model. Minimization of errors was initiated by providing initial guesses for each kinetic parameter. The best estimates were obtained using the MATLAB toolbox fminsearch, which is based on the Nelder–Mead optimization method.

The yield of LA on a molar base (YLA) is defined as the ratio of the LA concentration in the reaction product (C_{LA}) and the initial concentration of the C6-sugars in the matured coconut water (C_{C6,0}):

$$Y_{LA} \text{(mol %)} = \frac{C_{LA}}{C_{C6,0}}$$  \hspace{1cm} (1)

C_{C6,0} is the sum of the available C6-sugar monomers (glucose and galactose) in the coconut water. It is also possible to define the yield of LA on a weight base (Y_{LA,wt}), which is defined as the mass ratio of LA and the available C6-sugars in the coconut water.

$$Y_{LA,wt} \text{(wt%)} = \frac{C_{LA} \times M_{LA}}{C_{C6,0} \times M_{C6,sugar}}$$  \hspace{1cm} (2)

the terms M_{LA} and M_{C6-sugars} represent the molecular weight of LA (116 g mol\(^{-1}\)) and C6-sugars (180 g mol\(^{-1}\)), respectively. Chemical balance (1) to (4) showed the chemical reaction of glucose to levulinic acid. The equation (5) to (16) is the mathematical kinetic model of levulinic acid production from glucose that was for simulation in MATLAB R2013b (Simulink).
\[ R_1 = k_{1G}(C_{GLC})^{aG}(C_{H^+})^{aG} \] (7)
\[ R_2 = k_{2G}(C_{GLC})^{bG}(C_{H^+})^{bG} \] (8)
\[ R_3 = k_{1H}(C_{HMFP})^{aH}(C_{H^+})^{aH} \] (9)
\[ R_4 = k_{2H}(C_{HMFP})^{bH}(C_{H^+})^{bH} \] (10)

\[ K_{1G} = k_{1RG} \exp \left[ -\frac{(E_{1G/R})}{T} \frac{1}{T} \frac{1}{T} \right] \] (11)
\[ K_{2G} = k_{2RG} \exp \left[ -\frac{(E_{2G/R})}{T} \frac{1}{T} \frac{1}{T} \right] \] (12)
\[ K_{1H} = k_{1RH} \exp \left[ -\frac{(E_{1H/R})}{T} \frac{1}{T} \frac{1}{T} \right] \] (13)
\[ K_{2H} = k_{2RH} \exp \left[ -\frac{(E_{2H/R})}{T} \frac{1}{T} \frac{1}{T} \right] \] (14)

\[ C_{H^+} = C_{H_2SO_4} + \frac{1}{2} \left( -K_{a,HSO_4} + \sqrt{(K_{a,HSO_4}^2 + 4C_{H_2SO_4}K_{a,HSO_4})} \right) \] (15)

\[ \frac{dC_{GLC}}{dt} = -(R_1 + R_2) \] (16)
\[ \frac{dC_{HMFP}}{dt} = R_1 - (R_3 + R_4) \] (17)
\[ \frac{dC_{LA}}{dt} = R_3 \] (18)
3. Results and Discussion
Levulinic acid was produced from sugar through acid hydrolysis along with heating. In this process, glucose was decomposed into hydroxymethyl furfural (HMF) followed by conversion to levulinic acid and formic acid. Sulfuric acid is a well-known catalyst in process but its efficiency may vary depending on the raw material [11] and reaction conditions such as temperature and acid concentration. Thus, a preliminary study was conducted prior to simulation modelling on levulinic acid production by manipulating reaction time and catalyst concentration. The concentration profile of acid sulphuric-catalysed hydrolysis on matured coconut water are given in table 2 where the reactions were carried for 30 minutes at 100°C. For simple sugars such as glucose and fructose, temperature ranging from 90-120°C was sufficient for their conversion to levulinic acid [8]. At the end of reaction, 10% of 1 M sulfuric acid mixture gave the most production of levulinic acid. The yield however decreases when lower concentration of acid were used and same pattern was observed as portion of coconut water in mixture decrease. Even though 10% of 1 M sulfuric acid has the highest product, the yield percentage was relatively low (less than mol 1%). The possible explanation for this finding is duration for monomeric C6-sugars’ reduction was not long enough for reaction. This is consistent with Rackemann [3] which suggest that an improvement trend in the yield of levulinic acid will happen by increasing catalyst concentration and response time. In further experiment, ratio of 9:1 old coconut water to sulfuric acid was used.

Table 2. The yield of levulinic acid in different ratio of coconut water to sulfuric acid mixture

| Ratio    | Concentration of acid catalyst (M) | Yield of levulinic acid (mol%) |
|----------|-----------------------------------|--------------------------------|
| 9:1      | 0.50                              | 0.096                          |
| 8:2      | 0.50                              | 0.094                          |
| 7:3      | 0.50                              | 0.054                          |
| 9:1      | 0.75                              | 0.102                          |
| 8:2      | 0.75                              | 0.094                          |
| 7:3      | 0.75                              | 0.093                          |
| 9:1      | 1.00                              | 0.134                          |
| 8:2      | 1.00                              | 0.098                          |
| 7:3      | 1.00                              | 0.094                          |

To determine the other potential catalyst and enhance the levulinic acid production, a comparison was made between three types of strong acids that were hydrochloric acid (HCl), sulfuric acid (H2SO4) and phosphoric acid (H3PO4). As these acids were diluted into different concentrations, the acid concentration of 1.0 M gave the highest yield respectively (table 3).

HCl and H2SO4 catalyst gave higher yield than H3PO4 due to its acidity strength. These acids have different dissociation constant (pKa) (HCl: -7, H2SO4: -3, H3PO4: 2.1) where the acidity strength inversely proportional to the pKa value. Furthermore, the experiments of the reaction time parameters have been performed with different time ranges; 15, 30, 45 and 60 minutes. Thus, sulfuric acid was used in further experiment. Figure 2, 3 and 4 show the amount levulinic acid and formic acid formed from sugars degradation of matured coconut water in interval 15 minutes of reaction times.
Table 3. Average yield of levulinic acid with different concentration of acid catalyst

| Concentration of acid catalyst | Yield of levulinic acid, LA (mol %) | Yield of formic acid, FA (mol %) |
|-------------------------------|-----------------------------------|---------------------------------|
| 0.50M H₂SO₄                   | 0.046                             | 0.009                           |
| 0.75M H₂SO₄                   | 0.052                             | 0.016                           |
| 1.00M H₂SO₄                   | 0.071                             | 0.028                           |
| 0.50M HCl                     | 0.046                             | 0.001                           |
| 0.75M HCl                     | 0.053                             | 0.006                           |
| 1.00M HCl                     | 0.079                             | 0.011                           |
| 0.50M H₃PO₄                   | 0.039                             | 0.005                           |
| 0.75M H₃PO₄                   | 0.046                             | 0.010                           |
| 1.00M H₃PO₄                   | 0.057                             | 0.013                           |

Figure 2. The amount of levulinic and formic acid produced from matured coconut water catalyzed by 0.5 M H₂SO₄

Figure 3. The amount of levulinic and formic acid produced from matured coconut water catalyzed by 0.75 M H₂SO₄
Figure 4. The amount of levulinic and formic acid produced from matured coconut water catalyzed by 1.0 M H$_2$SO$_4$

The levulinic acid production increased as the reaction time prolong in these three acid concentrations but after 60 minutes of reaction, a decline pattern was found in both 0.75 M and 1 M H$_2$SO$_4$. These finding were however contradicting with Rackemann (2014) who stated that improvement trend of yield will be seen by increasing catalyst concentration and response time. These unpredicted finding might due to error occurred during experimental setup or formation of humin might has begun once the reaction time was extended to one hour.

A simulation model is a mathematical model that tries to resemble a real life system through use of computer software. For the simulation of levulinic acid production, a modelling system was developed using the MATLAB R2012b simulink software. The system has been build base on the equation (7)-(18) that enable the control catalyst concentration input along with the reaction time. The kinetic parameters used in this simulation were regulated based on Girisuta et al. [8] by assuming concentration of HMF is equal to concentration of acid catalyst where it gives the value of $k_{1H} = 0.0029$, $C_{IMF} = 0.11$, $aH = 0.88$, $aH = 1.38$ and the concentration of acid is 1.0 M H$_2$SO$_4$ (Figure 5).

Figure 6 depicts an increasing trend of levulinic acid production for the first half hour consistent with the experimental trend and the production was predicted to increase as it reaches 2 hours of reaction while remain constant by slightly decrease for the rest of reaction time. To validate this model, experiment was repeated with the suggested conditions and percentage of differences was calculated. The differences that less than 20 percent was considered as a good model.

Figure 5. Simulink model of levulinic acid production
Figure 6. Predicted yield percentage of levulinic acid according to simulation model

4. Conclusion
The 9:1 ratio of matured coconut water to acid catalyst was selected as the best ratio to carry on the sequential experiment. Both HCl and H₂SO₄ are strong acids that gave high levulinic acid amount at operating temperature 100ºC and 30 minutes reaction time. Yet, matured coconut water which commonly as agrowaste in Malaysia has the potential to produce levulinic acid. As compared with previous studies by Rackemann and Girisuta, the levulinic acid finding in this research was significantly low. Sophisticated technology is one of the factor that contribute to their high results. Simulation of levulinic acid production systems has been developed using MATLAB R2013b (Simulink) through generating kinetic model from several related equations. Although the simulation and experimental graph were slightly different, some errors might occur during these processes.

References
[1] Frankiewicz A 2016 Overview of 4-oxopentanoic (levulinic) acid production methods – an intermediate in the biorefinery process Chemik 70(4) 206–08
[2] Huber G W, Iborra S and Corma A 2006 Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering Chem Rev 106(2) 4044–98
[3] Rackemann D W 2014 Production of Levulinic Acid and Other Chemicals From Sugarcane Fibre (Queensland: PhD thesis Queensland University of Technology) p 264
[4] Prades A, Dornier M, Diop N and Pain J P 2012 Coconut water uses, composition and properties: a review Fruits 67(2) 87–107
[5] Bozell J J and Petersen G R 2010 Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. Green Chemistry 12(4) 539
[6] Watson L J and Connors C G 2008 Furfural - A value adding opportunity for the Australian Sugar Industry Proceedings of the Australian Society of Sugar Cane Technology 30 429–36
[7] Fang Q and Hanna M A 2002 Experimental studies for levulinic acid production from whole kernel grain sorghum. Bioresource Technology 81(3) 187–92
[8] Girisuta B, Danon B, Manurung R, Janssen L P and Heeres H J 2008 Experimental and kinetic modelling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid Bioresource Technology 99 8367–75
[9] Tarabanko V E, Chernyak M Y, Aralova S V and Kuznetsov B N 2002 Kinetics of levulinic acid formation from carbohydrates at moderate temperatures. Reaction Kinetics and Catalysis Letters 75(1) 117–26
[10] Chen H, Yu B. and Jin S 2011 Production of levulinic acid from steam exploded rice straw via solid superacid $\text{S}_2\text{O}_8\text{S}_2$/$\text{ZrO}_2$-$\text{SiO}_2$-$\text{Sm}_2\text{O}_3$ Bioresource Technology 102(3) 3568–70

[11] Meinita M D N, Hong Y K and Jeong G T 2012 Comparison of sulfuric and hydrochloric acids as catalysts in hydrolysis of Kappaphycus alvarezii (cottonii) Bioprocess Biosyst. Eng. 35(1-2) 123-28