

# Effects of Ethanol:Water Ratio and Reaction Time on Ethyl Levulinate Synthesis from Oil Palm Empty Fruit Bunch (OPEFB)

Christopher Widjaja<sup>1,\*</sup>, Heriyanti<sup>1,2</sup>, Kritisana Namhaed<sup>3</sup>, Misri Gozan<sup>1,4,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia

<sup>2</sup>Department of Industrial Chemistry, Faculty of Science and Technology, Universitas Jambi, Jambi 36361, Indonesia

<sup>3</sup>INP, Laboratoire de Génie Chimique, 4 allée Emile Monso, CS 84234, 31 432 Toulouse Cedex 4, France

<sup>4</sup>Research Centre for Biomass Valorization-Universitas Indonesia (RCBV-UI), Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia

**Abstract.** World energy consumption continues to escalate annually in line with current world development. Meeting this burgeoning demand necessitates the exploration of renewable energy. Biofuel is one of the promising alternatives for renewable energy sources. However, biofuel has a disadvantage in its lower overall performance than fossil fuel. The application of additives such as ethyl levulinate emerges as a potential solution to enhance biofuel performance. This research aims to investigate the effect of ethanol:water ratio and reaction time on the formation of ethyl levulinate from Oil Palm Empty Fruit Bunch (OPEFB). The OPEFB to be utilized was pretreated with 3% NaOH at a solid-to-liquid ratio of 1:8. The reaction was conducted at 120°C, with varying ethanol:water ratio and reaction time in the presence of H<sub>2</sub>SO<sub>4</sub> as the catalyst. The reaction products were extracted using ethanol and analyzed with gas chromatography–mass spectrometry. The optimum reaction conditions obtained were 90 minutes and ethanol:water ratio of 99.1:0.9, resulting in a yield of 1.01%.

## 1 Introduction

World energy consumption increased by 5%, But 80% of all energy is still produced from non-renewable sources like crude oil, natural gas, and coal [1]. Besides the mentioned energy sources running out, non-renewable fuel sources have disadvantages such as greenhouse gas production. Greenhouse gases like carbon dioxide can cause global warming. Another problem stems from burning sulfur-containing coals can produce sulfur dioxide gas. When combined with water, sulfur dioxide can produce acid rain that harms living beings [2].

---

\* Corresponding author: [christopher.wj15@gmail.com](mailto:christopher.wj15@gmail.com); [mgozan@ui.ac.id](mailto:mgozan@ui.ac.id)

Biofuels boast a carbon-neutral profile and are derived from abundantly available plant materials [3]. However, biofuels have some limitations when compared to fossil fuels. One notable drawback is lower performance when used in cold temperatures [4,5]. Furthermore, biofuel has characteristics such as lower heating value, viscosity, and density than fossil fuel [6]. This causes poor atomization characteristics inside the engine, causing injector clogging, poor spray characteristics inside the combustion chamber, and incomplete combustion. Consequently, the application of additives in biofuels have an important role in overcoming biofuel limitations.

Ethyl levulinate is a promising biofuel additive, particularly enhancing low-temperature operation performance. Some researchers have proved that there is a performance boost at low temperatures when ethyl levulinate is added to biofuel [4,7]. Ethyl levulinate can be synthesized through the esterification reaction of levulinic acid and ethanol. However, the low production of levulinic acid, due to its multi-step reaction process, entails significant material costs associated with monosaccharide production from biomass and high separation and purification expenses [8,9].

Ethyl levulinate can be derived from cellulose liquefaction that is sourced from lignocellulosic biomass. Among the readily accessible lignocellulosic sources is open empty palm fruit bunch (OPEFB). Previous works have been done to make use of OPEFB, such as to produce bioplastic [10,11]; cellulase [12] and levulinic acids [13]. OPEFB remains underutilized despite its abundant availability. OPEFB has only been utilized as a fuel source and fertilizer [9]. OPEFB has cellulose content ranging from 36.67% to 55.75% [14,15]. The high cellulose content makes OPEFB a promising substrate for ethyl levulinate production.

This research aims to study the effects of ethanol:water ratio and reaction time to ethyl levulinate formation. This research also aims to increase OPEFB utilization.

## 2 Materials and Method

### 2.1 Raw Materials

OPEFB was locally sourced from Tangerang, Banten, Indonesia. OPEFB was washed and dried in the open air for 72 hours. The OPEFB was on the ground to 40 – 50 mesh size with a Retsch SM 2000 ball mill. Ground OPEFB was delignified by soaking OPEFB in 3% NaOH solution with a ratio of 1:8 between the OPEFB and NaOH solution at a temperature of 110 °C for 45 minutes [16]. Delignified OPEFB was washed, dried, and stored in a closed container. The delignified OPEFB that are utilized in this study has cellulose, hemicellulose, and lignin content of 26.94%, 20.59%, and 5.01%, respectively. Ethyl levulinate, ethanol 99%, H<sub>2</sub>SO<sub>4</sub>, and NaOH was obtained from Merck. Demineralized water is used throughout the research process.

### 2.2 Experimental Procedure

The synthesis of ethyl levulinate was conducted using an 800 ml autoclave reactor. In a typical experimental run, 4 grams of delignified OPEFB were introduced into the reactor. A mixture consisting of 40 ml of ethanol and water with varying ratios was subsequently added to the reactor. Additionally, 1 ml of H<sub>2</sub>SO<sub>4</sub> 2 M was used as the catalyst. The reactor was heated with a heating jacket controlled by an electric heater and a thermostat. The reaction was carried out at 120 °C with varied reaction time and constant stirring. The reaction time variations used were 30, 60, 90, 120, and 150 minutes, while the variations in the ratio of ethanol and water were pure ethanol, 80:20, 60:40, 40:20, and 20:80. After the reaction, the

reactor was cooled until the temperature reading reaches ambient temperature. Reaction products were extracted using 40 ml of ethanol with a temperature of 60 °C for 1 hour.

### 2.3 Analysis Method

The extracted reaction products were analyzed using PerkinElmer gas Chromatograph Clarus 680 gas chromatography and PerkinElmer Spectrometer Clarus SQ 8 T mass spectrometer.

### 2.4 Yield Calculation

The yield of ethyl levulinate formation was calculated using the following equation:

$$\%yield = \frac{\text{formed ethyl levulinate mass}}{\text{cellulose mass}} \quad (1)$$

The cellulose mass was calculated by multiplying the OPEFB sample by its cellulose content in OPEFB. The cellulose mass obtained was 1.0775 grams.

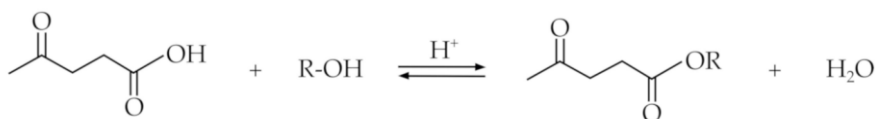
## 3 Results and Discussion

### 3.1 The Effects of Reaction Time

**Table 1.** Reaction Time Effects to Ethyl Levulinate Formation

Reaction time (min)	Ethyl levulinate (mg)	Yield (%)
30	2.147	0.20
60	9.557	0.89
90	10.872	1.01
120	10.602	0.98
150	10.181	0.94

Table 1 showed the effect of reaction time on ethyl levulinate formation from OPEFB. The solvent used was pure ethanol. The maximum yield of ethyl levulinate was achieved at a reaction time of 90 minutes, with a yield of 1.01%. As the reaction time extended to 120 and 150 minutes, a decline in yield was observed. This phenomenon may occur due to the equilibrium state has been achieved within 90 minutes, resulting in an equal rate of ethyl levulinate formation and its degradation into levulinic acid and ethanol (Figure 1).



**Figure 1.** Equilibrium reaction for the formation of ethyl levulinate

This observation is consistent with previous studies conducted by Chang et al. and Le Van Mao et al., where the production of ethyl levulinate from lignocellulosic biomass using  $H_2SO_4$  as a catalyst ranged from 36 minutes to 102 minutes [8,17,18]. It is also stated that ethyl levulinate yield decreases as the reaction exceeds the optimum reaction time. This is caused by side products accumulation from other reactions that can inhibit the main reactions like humins [8,17,19].

### 3.2 The Effects of Ethanol:Water Ratio

Ethyl levulinate synthesis was carried out for 90 minutes for all variations of the ethanol water ratio. For every 1 ml of  $H_2SO_4$  2 M catalyst used, 0,9 ml of water must be accounted for. This causes the ratio between ethanol and water to be recalculated. The new ethanol:water ratio used is stated in Table 2.

**Table 2.** Ethanol:Water Ratio Effects to Ethyl Levulinate Formation

Ethanol:water ratio	Ethyl levulinate (mg)	Yield (%)
99.1:0.9	10.872	1.01
79.1:20.9	8.504	0.79
59.1:40.9	3.723	0.35
39.1:60.9	0.288	0.03
19.1:80.9	0	0

As observed in Table 2, the yield of ethyl levulinate formation yield exhibits a decline as the ethanol ratio decreases. Water in the system does not only come from reactants and catalyst that are being used. Water also comes from the side product of the esterification reaction. Additionally, water is produced through the dehydration of fructose and ethanol. An increase in water content within the system tends to favor the degradation of ethyl levulinate into levulinic acid and ethanol [20,21].

The addition of water also results in a decrease the  $H_2SO_4$  catalyst concentration employed. The reduced catalyst concentration can lead to lower catalyst performance, consequently leading to a decrease in ethyl levulinate production. Some research proves that catalyst concentration is important for levulinic acid formation, which serves as a precursor to ethyl levulinate. In the research, levulinic acid production increases as catalyst concentration used increases. [22–25].

## 4 Conclusion

This research has successfully obtained ethyl levulinate from OPEFB with a variation of reaction time and ethanol:water ratio. From the research, it can be concluded that maximum ethyl levulinate formation yield recorded is 1.01% with reaction time of 90 minutes and ethanol:water ratio of 99.1:0.9. Ethyl levulinate formation yield will increase as reaction time length is increased to the optimum point. Ethyl levulinate formation yield will decrease as ethanol ratio decreases in the ethanol and water mixture.

This work was supported by the Hibah Publikasi Terindeks Internasional (PUTI) Pascasarjana Universitas Indonesia Tahun Anggaran 2023—2024. Nomor: NKB-266/UN2.RST/HKP.05.00/2023 The authors acknowledge Badan Riset dan Inovasi Nasional for the supporting equipment. The authors also thank every party that support the research.

## References

- [1] World Energy Consumption Statistics | Enerdata, (2022).  
<https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html>  
(accessed November 22, 2022).
- [2] N.K. Shammass, L.K. Wang, M.-H.S. Wang, Sources, Chemistry and Control of Acid Rain in the Environment, in: *Handb. Environ. Waste Manag., WORLD SCIENTIFIC*, **1–26** (2020).
- [3] O. Awogbemi, D.V.V. Kallon, E.I. Onuh, V.S. Aigbodion, An Overview of the Classification, Production and Utilization of Biofuels for Internal Combustion Engine Applications, *Energies* **14** **5687** (2021).
- [4] H. Joshi, B.R. Moser, J. Toler, W.F. Smith, T. Walker, Ethyl levulinate: A potential bio-based diluent for biodiesel which improves cold flow properties, *Biomass Bioenergy* **35** **3262–3266** (2011).
- [5] A.Z. Mendiburu, C.H. Lauermaann, T.C. Hayashi, D.J. Mariños, R.B. Rodrigues Da Costa, C.J.R. Coronado, J.J. Roberts, J.A. De Carvalho, Ethanol as a renewable biofuel: Combustion characteristics and application in engines, *Energy* **257** **124688** (2022).
- [6] S. Madiwale, A. Karthikeyan, V. Bhojwani, A Comprehensive Review of Effect of Biodiesel Additives on Properties, Performance, and Emission, *IOP Conf. Ser. Mater. Sci. Eng.* **197** **012015** (2017).
- [7] D. Unlu, N. Boz, O. Ilgen, N. Hilmioglu, Improvement of fuel properties of biodiesel with bioadditive ethyl levulinate, *Open Chem.* **16** **647–652** (2018).
- [8] D. Di Menno Di Bucchianico, Y. Wang, J.-C. Buvat, Y. Pan, V. Casson Moreno, S. Leveneur, Production of levulinic acid and alkyl levulinates: a process insight, *Green Chem.* **24** **614–646** (2022).
- [9] J. Han, J. Kim, Process Simulation and Optimization of 10-MW EFB Power Plant, in: *Comput. Aided Chem. Eng.*, Elsevier, **723–729** (2018).
- [10] Rahmayetty, Y. Whulanza, Sukirno, S.F. Rahman, E.A. Suyono, M. Yohda, M. Gozan, Use of *Candida rugosa* lipase as a biocatalyst for L-lactide ring-opening polymerization and polylactic acid production, *Biocatal. Agric. Biotechnol.* **16** **683–691** (2018).
- [11] Yustinah, N. Hidayat, R. Alamsyah, A.M. Roslan, H. Hermansyah, M. Gozan, Production of polyhydroxybutyrate from oil palm empty fruit bunch (OPEFB) hydrolysates by *Bacillus cereus* suaeda B-001, *Biocatal. Agric. Biotechnol.* **18** **101019** (2019).
- [12] S.Z. Amraini, L.P. Ariyani, H. Hermansyah, S. Setyahadi, S.F. Rahman, D.-H. Park, M. Gozan, Production and characterization of cellulase from *E. coli* EgRK2

- recombinant based oil palm empty fruit bunch, *Biotechnol. Bioprocess Eng.* 22 **287–295** (2017).
- [13] M. Gozan, J.R.H. Panjaitan, D. Tristantini, R. Alamsyah, Y.J. Yoo, Evaluation of Separate and Simultaneous Kinetic Parameters for Levulinic Acid and Furfural Production from Pretreated Palm Oil Empty Fruit Bunches, *Int. J. Chem. Eng.* 2018 **1–12** (2018).
- [14] N. Hidayah, I.U. Wusko, Characterization and Analysis of Oil Palm Empty Fruit Bunch (OPEFB) Waste of PT Kharisma Alam Persada South Borneo, *Maj. Obat Tradis.* 25 (2020).
- [15] D. Setyaningsih, Uju, N. Muna, Isroi, N.B. Suryawan, A.A. Nurfauzi, Cellulose nanofiber isolation from palm oil Empty Fruit Bunches (EFB) through strong acid hydrolysis, *IOP Conf. Ser. Earth Environ. Sci.* 141 **012027** (2018).
- [16] A.A. Kamoldeen, C.K. Lee, W.N. Wan Abdullah, C.P. Leh, Enhanced ethanol production from mild alkali-treated oil-palm empty fruit bunches via co-fermentation of glucose and xylose, *Renew. Energy* 107 **113–123** (2017).
- [17] C. Chang, G. Xu, X. Jiang, Production of ethyl levulinate by direct conversion of wheat straw in ethanol media, *Bioresour. Technol.* 121 **93–99** (2012).
- [18] R. Le Van Mao, Q. Zhao, G. Dima, D. Petraccone, New Process for the Acid-Catalyzed Conversion of Cellulosic Biomass (AC3B) into Alkyl Levulinates and Other Esters Using a Unique One-Pot System of Reaction and Product Extraction, *Catal. Lett.* 141 **271–276** (2011).
- [19] Q.-W. Zhang, L.-G. Lin, W.-C. Ye, Techniques for extraction and isolation of natural products: a comprehensive review, *Chin. Med.* 13 **20** (2018).
- [20] J. Tan, Q. Liu, L. Chen, T. Wang, L. Ma, G. Chen, Efficient production of ethyl levulinate from cassava over Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> catalyst in ethanol–water system, *J. Energy Chem.* 26 **115–120** (2017).
- [21] G.-Z. Xu, C. Chang, W.-N. Zhu, B. Li, X.-J. Ma, F.-G. Du, A comparative study on direct production of ethyl levulinate from glucose in ethanol media catalysed by different acid catalysts, *Chem. Pap.* 67 (2013).
- [22] S. Kang, J. Fu, N. Zhou, R. Liu, Z. Peng, Y. Xu, Concentrated Levulinic Acid Production from Sugar Cane Molasses, *Energy Fuels* 32 **3526–3531** (2018).
- [23] L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang, Y. Gong, Catalytic Conversion of Cellulose to Levulinic Acid by Metal Chlorides, *Molecules* 15 **5258–5272** (2010).
- [24] M. Signoretto, S. Taghavi, E. Ghedini, F. Menegazzo, Catalytic Production of Levulinic Acid (LA) from Actual Biomass, *Molecules* 24 **2760** (2019).
- [25] Z. Zhi, N. Li, Y. Qiao, X. Zheng, H. Wang, X. Lu, Kinetic study of levulinic acid production from corn stalk at relatively high temperature using FeCl<sub>3</sub> as catalyst: A simplified model evaluated, *Ind. Crops Prod.* 76 **672–680** (2015).