

## Chemical processing of lingo-cellulosic biomass sugars for biofuel

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### Abstract

Bio-refineries convert biomass into high-value chemicals, which is essential for long-term development. One of the most significant raw sources for bio-refineries is Ligno-Cellulosic Biomass (LCB), which comprises polysaccharides and aromatic polymers. Effective pretreatment procedures may extract hexose and pentose sugars from LCB, which can then be turned into high-value chemicals and biofuels including 5-hydroxymethylfurfural (HMF), Levulinic Acid (LA),  $\gamma$ -valerolactone (GVL), Ethyl Levulinate (EL), and 5-ethoxymethylfurfural (EMF). EMF has the highest cetane number and the best oxidation stability among these biofuels. The mechanism of various major stages of EMF synthesis from LCB-derived sugars, as well as recent research developments on acid catalysts employed in this reaction. The effect of mono and bi-functional acid catalyst characteristics and structures on the selectivity of EMF from glucose was examined, as well as the effect of reaction conditions on EMF yield.

**Keywords:** Bio-refineries; Biomass; Oxidation; Fluorescence

### Introduction

The widespread usage of fossil fuels has resulted in energy depletion as well as major environmental issues (e.g., greenhouse effect and acid rain). For a healthier living environment, it is critical to produce green renewable energy to replace fossil fuels. Ligno-Cellulosic Biomass (LCB) is a common renewable energy source, with a global production of around 12 billion tons per year [1]. It is mostly made up of cellulose and hemicellulose components coated in lignin. Among them, cellulose is a biopolymer that connects large glucose units via 1,4-glycosidic linkages and makes up 38%–50% of LCB. By hydrolyzing cellulose, a substantial amount of glucose may be produced. Many researchers were interested in converting glucose into high-value-added compounds. Glucose may be converted into high-value-added fuels and fine chemicals by catalytic processes such as dehydration, hydrogenation, hydrolysis, alcoholysis, and etherification (e.g., 5-hydroxymethylfurfural (HMF), 5-ethoxymethylfurfural (EMF), levulinic acid, and ethyl levulinate).

Furan derivatives such as furfural, furfuryl alcohol, HMF, EMF, and 2, 5-dimethylfuran has showed promise as fine chemicals and alternative fossil fuels. EMF has a greater boiling point (235°C), a higher energy density (30.3 MJ/L) than ethanol (23.5 MJ/L), and a lower flash point (about 110°C) than the other furan derivatives. As a result, it has been regarded as one of the best gasoline additives for the future. When 17 wt% EMF was employed as an additive in a gasoline engine, the engine was able to function more consistently and generate less hazardous particles and sulphides (with a 16% reduction in soot). EMF has also been employed as a reaction substrate in the synthesis of a number of industrially important compounds, including 5-ethoxymethylfurfuryl alcohol, 2, 5-diethoxymethylfuran, and cyclopentenone [2]. In general, EMF may be produced with an acceptable yield (70–90%) from HMF and ketoses (e.g., fructose, inulin, and sucrose). This high-priced feedstock's, however, restricted the industrial-scale manufacturing of EMF.

### EMF Production Using LCB-Derived Sugars

**Synthesis Routes:** Through a multi-step chemical reaction, EMF may be made from glucose or cellulose. EMF may be produced in three ways from glucose. The traditional Path I start with glucose, which is isomerized to make fructose, then fructose dehydration

produces HMF, and lastly HMF is etherified to produce EMF [3-4]. The isomerization of glucose, which generally involves the presence of Lewis acid, is the most critical stage in this process. With ethyl-D-fructofuranoside (EDFF) as an intermediary transit, there are two possible alternative pathways. Fructose combines with ethanol in an acidic solution to make EDFF, which is subsequently dehydrated to produce EMF. In an acid medium, glucose and ethanol are combined to form ethyl-D-glucopyranoside (EDGP), which is subsequently isomerized to EDFF and ultimately dehydrated ( $-3\text{H}_2\text{O}$ ) to yield EMF. For the time being, the majority of EMF is collected via Path I for the following reasons:

- Compare and contrast Path I with Path II. Fructose, on the other hand, is more likely to be converted to HMF (Path I) or EDFF (Path II). When Bronsted acid is present, fructose is more likely to be dehydrated to create HMF (Path I) rather than etherified with ethanol to form EDFF (Path II).
- Compare and contrast Path I with Path III. When Bronsted acid and Lewis acid are present at the same time, glucose is frequently isomerized to fructose. Although the DFT calculations demonstrate that the maximum energy barriers required for Path I (17.7 kcal/mol) and II (20.8 kcal/mol) are equal when just Bronsted acid is present, the thermodynamic reaction favors Path I. Further conversion of the intermediate EDGP in Path III is problematic.

**Synthesis Mechanism:** Multiple chemical mechanisms, especially cascade reactions, are required to convert cellulose to EMF. Cellulose has a condensed structure and is a high molecular polymer with many glucose monomers joined by  $\beta$ -1,4-glycosidic linkages and axial hydrogen bonds. As a result, the hydrolysis of cellulose in Path I's initial step is a significant challenge that must be solved [5-6]. Bronsted acid has been demonstrated in several experiments to disrupt cellulose's  $\beta$ -1, 4-glycosidic linkages. The proton of the Bronsted acid site attacks the oxygen atom of the  $\beta$ -1, 4-glycosidic bond [7]. The C-O connection between the two glucose molecules is then broken, releasing glucose and the intermediate glucose-ion. Finally, the hydroxyl group from water attaches to the glucose-ion intermediate's exposed carbon to produce glucose. The water's liberated protons then take part in the following hydrolysis step.

The isomerization of glucose into fructose, the second step in Path I, is the most significant step in determining EMF yield. Glucose is converted to fructose via Lewis acid sites, according to several studies. Lewis acid breaks the  $\text{C}_1\text{-O}_5$  bond in glucose, resulting in a linear glucose molecule. On linear glucose, the oxygen atoms of  $\text{C}_1$  and  $\text{C}_2$  align with the Lewis acid core [8-9]. The hydrogen on  $\text{C}_2$  is then transferred to  $\text{C}_1$ , completing the aldehyde-ketone conversion between  $\text{C}_1$  and  $\text{C}_2$ , resulting in linear fructose. Finally, a C-C bond connects  $\text{C}_2$ 's oxygen to  $\text{C}_5$  to produce a fructose molecule.

Fructose creates HMF in the third stage by dehydrating  $3\text{H}_2\text{O}$  molecules under acidic circumstances.  $\text{C}=\text{C}$  is generated between  $\text{C}_1$  and  $\text{C}_2$  when the hydroxyl group on  $\text{C}_2$  is protonated to release the initial  $\text{H}_2\text{O}$ . The hydroxyl group on  $\text{C}_3$  is then protonated, resulting in the release of the second  $\text{H}_2\text{O}$ . Meanwhile, the  $\text{C}=\text{C}$  link between  $\text{C}_1$  and  $\text{C}_2$  is broken, the aldehyde group forms at  $\text{C}_1$ , and  $\text{C}=\text{C}$  between  $\text{C}_2$  and  $\text{C}_3$  is created. Finally, the hydroxyl group on  $\text{C}_4$  is protonated, releasing the third  $\text{H}_2\text{O}$ , and a  $\text{C}=\text{C}$  bond is formed between  $\text{C}_4$  and  $\text{C}_5$  to produce HMF. Following that, HMF is etherified to EMF in the presence of ethanol.

### Factors Influencing EMF Yield from LCB-Derived Sugars

Many LCB-derived sugars and substances, including as cellulose, cellobiose, and glucose, have been employed to convert into EMF. The order of EMF yield from these substrates was glucose > cellobiose > cellulose > LCB. Due to the varied number of reaction stages, only moderate or low EMF yields can be produced from these raw materials [10-12]. HMF as a feedstock (high EMF yield) requires only one step, but cellulose (low EMF yield) requires four. Meanwhile, the protracted chemical reaction process resulted in a rise of by-products, also known as humins. As a result, a lot of research has gone into designing more efficient catalytic systems that can get better EMF yields from glucose or glucose-based carbohydrates.

**Mono-functional Acid Catalysts:** Many mono-functional (Bronsted or Lewis) acid catalysts, including as  $\text{H}_2\text{SO}_4$ , metal salts,  $\text{SO}_3\text{H}$ -based catalyst, and ionic liquid, are currently being developed to catalyze the production of EMF from glucose. In terms of synthesis methods, when just Bronsted acid is present, employing glucose as a substrate creates very little EMF [13]. Despite this, several investigations have revealed that employing glucose (7.46% yield), cellobiose (19.8% yield), and cellulose (3.05% yield) as raw materials, a spot of EMF may be detected in the presence of Bronsted acid. One probable explanation is that in Bronsted acid, glucose forms a bit intermediate 3-deoxyglucosone, which is subsequently dehydrated to generate HMF, and then etherified to form EMF. Furthermore, Bronsted acid and protonated ethanol can open the glucose ring to generate intermediate 1, 2-enediol, which subsequently isomerizes to fructose, allowing EMF to be produced in the following phase.

When there is just Lewis acid in the solution, glucose can provide a modest EMF yield (10%–40%). The difficulty to produce high EMF yield in the presence of a single Lewis acid might be due to the Lewis acid's inability to supply  $\text{H}^+$ , resulting in a low  $[\text{C}_2\text{H}_5\text{OH}_2]^+$  concentration in the system, which inhibits fructose dehydration and subsequent etherification processes. Meanwhile,

the EMF yields produced by catalyzing glucose with various metal salts varied greatly. Metal chlorides like  $\text{AlCl}_3$  and  $\text{CrCl}_3$  have EMF yields of 11.2% and 15.2%, respectively.

With metal sulphates  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Cr}_2(\text{SO}_4)_3$  as catalysts, the reaction system detected little EMF but a lot of EDGP (about 80% yield). As a result, the metal chloride is more favorable to glucose isomerization, whereas the metal sulphate is more conducive to glucose etherification [14]. Overall, mono-functional acid catalysts are unable to produce an acceptable EMF yield from glucose. The discovered bi-functional acid catalysts using Bronsted-Lewis acids, on the other hand, can get a lot of EMF out of glucose.

Bi-functional Acid Catalysts: Bronsted acid species  $\text{Al-O(H)-Si}$  (framework four-coordinate aluminum) are often found in zeolite molecular sieve catalysts, while Lewis acid species  $\text{Al}^+$  (framework three-coordinate aluminum) may be generated following high-temperature dealumination. For example, following high-temperature dealumination, ultra-stable Y zeolite (USY) and  $\beta$  zeolite (H- $\beta$ ) were utilized to catalyze the synthesis of EMF from glucose, yielding 39.5% and 41% EMF, respectively. Additionally, zeolite may be changed to improve EMF production. Sn- and Al- Lewis acid species are introduced into zeolite to produce MFI-Sn/Al, or  $\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4]$  and  $\text{SnCl}_4$  (Bronsted-Lewis acids) are concurrently introduced into zeolite to produce SBA-15. These catalysts may produce EMF from glucose with a middling yield. A pliable template the sulfonic acid group was supported by HIPE, and  $\text{Cr}^{3+}$  was used to make BFC-3 catalyst, which could be used to catalyze glucose and cellobiose, yielding 48.1% and 37.1 % EMF yields, respectively. Glycerol and glucose were also sulfonated into carbon spheres before being injected into  $\text{Zn}^-$  to make  $\text{Zn-SO}_3\text{H-GR-carbon}$  and  $\text{Zn-S-C}$ . They can both get incredible EMF yields from glucose (86.3% and 80.9%).

The catalytic efficiency of bi-functional acid catalysts varies greatly. The yields of EMF produced from glucose were variable while using the same Bronsted acid and different Lewis acids to construct distinct catalysts. For example, different metal species ( $\text{Zn}^-$ ,  $\text{Al}^+$ , and  $\text{Ni}^+$ ) were doped into the sulfonated carbon, resulting in different catalytic performances.  $\text{Zn-SC}$ ,  $\text{Al-SC}$ , and  $\text{Ni-SC}$  provided yields of 85.1%, 84.4% and 32.8 %, respectively, when EMF was preferentially generated from glucose. The discrepancy is due to the fact that the acidity given by  $\text{Ni}^+$  is lower than that of  $\text{Zn}^-$  and  $\text{Al}^+$ . Recent studies show that this kind of Lewis acid has an effect on EMF production. Meanwhile, the quantity of metal species in the catalyst had an effect on its performance, according to this study. The higher the number of different metals in the catalyst, the better the catalytic efficiency. Furthermore, selecting an appropriate Bronsted/Lewis acid ratio can increase EMF selectivity [15]. When the weak acid accounts for more in the ratio of strong/weak acid, it is detrimental to glucose isomerization, fructose dehydration, and HMF etherification, resulting in reduced EMF selectivity. When additional strong acids are present in the solution, however, the resultant EMF can be transformed into EL or humins via a ring-opening process. For getting EMF from glucose, the ratio of Bronsted/Lewis and strong/weak acids in bi-functional acid catalysts is particularly crucial.

## Conclusion

The advantages of LCB in the field of sustainable energy conversion are due to its richness, variety, and accessibility. In recent years, the methods and technology for producing EMF from LCB-derived sugars have been studied. The goal of these investigations is to design more efficient catalysts and reaction systems in order to boost EMF yield.

EMF is made from glucose, which is a common LCB-derived sugar. EMF is mostly synthesized via route I. When mono-functional acid catalysts are utilized, the EMF yield is often poor. The glucose isomerization phase (equivalent to Lewis acid) and low concentration of  $[\text{C}_2\text{H}_5\text{OH}_2]^+$  are thought to be the cause of this difficulty (corresponding to Bronsted acid). However, the newly discovered bi-functional (Bronsted-Lewis) acid catalysts may efficiently handle this difficulty, resulting in acceptable EMF yields from glucose. Meanwhile, the Lewis acid species, Bronsted/Lewis acid ratio, and strong/weak acid ratio in bi-functional acid catalysts all have a significant impact on EMF yield. In addition, advancements in EMF yield have been made by the adjustment of reaction conditions. The selectivity of EMF may be improved by using the right time, temperature, and concentration of co-solvent.

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