

Catalytic technologies for the complete conversion of lignocellulosic biomass into fuels and chemicals

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ABSTRACT

Biomass is an abundant and renewable carbon source from which fuels and a variety of chemicals can be produced. In recent years, several processes of catalytic conversion of lignocellulosic biomass have been developed, essentially aiming at using forest residues and agricultural wastes as raw materials.

In this work, Fenton's chemistry is being used to convert, at first, cellulose and hemicellulose components of lignocellulosic biomass into carboxylic acids and their corresponding ethyl esters. Representative of such carboxylic acids is levulinic acid, an important platform chemical. Highly energetic free radicals generated by the Fenton's reagent are believed to be the principal conversion species. Moreover, these radicals are strong enough to crack further the obtained lignin char, thus yielding other carboxylic (and dicarboxylic) acids and alkyl aromatics. The latter compounds may be used for tailoring the "green" bio-jet fuels.

Thus, complete conversion of lignocellulosic biomass can be achieved, showing the way to the sustainable exploitation of such raw materials.

Keywords: lignocellulosic biomass, catalytic conversion, Fenton's reagent, levulinic acid, lignin char depolymerization

1 Introduction

Bio-ethanol is one of the first products that are being chemically (and bio-chemically) derived from sugar-, starch- or cellulose-containing biomass materials. Other important platform chemicals such as levulinic acid, can also be derived from such raw materials. However, the use of lignocellulosic biomass such as wood or plant containing materials always needs special treatment techniques that, at first and essentially, consist of a "disruption-opening" of the protective layer of the third main biomass component, e.g. lignin. So far, such operational requirement has great incidence on the production cost of the final product. In fact, although the first process for the production of levulinic acid (called Biofine [1]) is technically feasible, its commercial development has encountered numerous problems including its relatively high production cost.

Several technologies for catalytic conversion of lignocellulosic biomass, all making use of Fenton's reagent, have recently been developed (AC3B for production of levulinic acid LA, and hydrocarbons [2]; BTCA for the production of LA, some shorter carboxylic acids and their ethyl esters [3]). The BTCA process uses Fenton's catalyst in slightly acidic medium to primarily treat the biomass and then, to crack cellulose and hemicellulose to LA and other products in accordance with the well-known acid catalysed reaction mechanism [1].

2 The BTCA (biomass-to-carboxylic acids) process

The use of Fenton's reagent considerably enhances the product yields of cellulose and hemicellulose in the AC3B process [4] because such Fenton-type catalyst (hydrogen peroxide and ferrous ions) is able to significantly increase the efficiency of the "disruption-opening (D-O)" of the biomass structure [3-5].

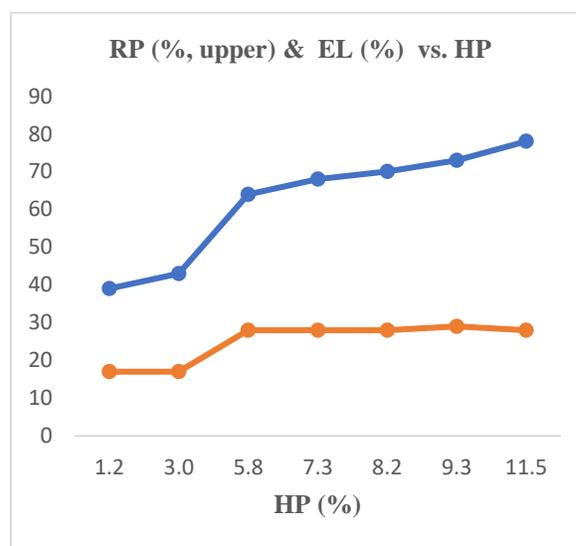


Figure 1: Total product yield (RP) and yield in ethyl levulinate (EL) versus hydrogen peroxide concentration (HP) in the one-pot process, AC3B.

This figure reports the yields of ethyl levulinate (EL) and the total liquid products (RP) vs. the H₂O₂ concentration (HP) of the reaction medium, the other component of the Fenton's reagent (Fe²⁺) being kept constant. It can be seen that an efficient D-O state is reached when the concentration of H₂O₂ of the biomass conversion slurry is equal or higher than 6.0 wt %.

In the more recently developed BTCA process, the Fenton's reagent treatment is completely separated from the acidic catalysed cracking step (Figure 2), so that it is now much easier to control the former step and thus to considerably decrease its negative effects on the overall process. The "D-O" action of the Fenton's reagent occurs only if the following conditions are fulfilled:

- a concentration of H₂O₂ higher than the threshold as mentioned earlier; and
- a temperature higher than 40/45 oC.

During such period of time, it is believed that very energetic hydroxyl free radicals are formed and the resulting "D-O" action on the biomass structure is fast and harsh: in fact, there is a drastic size reduction of the biomass material after a small "implosion" (rapid but limited increase in temperature and pressure, being an outward sign of the release of some large amount of energy). Nevertheless, the interactions of the Fenton's reagent with the biomass structure should involve species such as OH free radicals and also, electrophilic protonated H₂O₂ ions.

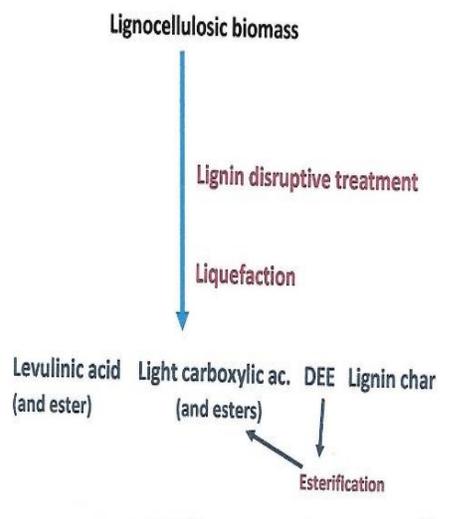


Figure 2: General scheme of the BTCA process

The BTCA procedure shows several different features, some being quite advantageous, when compared with the previously developed processes for the production of levulinic acid.

-Much lower consumption of H₂O₂ and very low temperature used in the pre-treatment phase (<150 oC);

-Use of a mixture of water/ethanol as solvent in the very mild acid cracking step, in order to: a) easily recover the ethyl esters of the carboxylic acids other than LA; b) considerably decrease

the production of unwanted diethyl ether. It is worth noting that in this case, LA and ethyl levulinate are both the main products;

-Recovery of much higher yields of (commercially valuable) ethyl esters of "other" carboxylic acids, due to the partial depolymerization of lignin, and thus obtaining of less lignin char.

Method	One-pot (a)	BTCA [3]
H ₂ O ₂ (g per 100g biomass)	20	14
Fe ²⁺ (mmol/100g biomass)	5.4	5.4
Yields of liquid products		
Ethyl levulinate	23	13
Levulinic acid	-	8
Ethyl formate	14	13
Ethyl acetate	13	12
Furfural	4	4
Methanol	3	4
Others	2	3
Total	59	57
Solid residue (approx.)		
Diethyl ether (g per 100 g biomass) ^(b)	38	5

Table 1: Product yields of the BTCA process versus those of previous process (biomass used = spruce chips, dried: < 6 wt % moisture).

(a) See procedure in reference [2]

(b) Being produced directly from ethanol

Therefore, preliminary economic assessment of the BTCA process results in a production cost for levulinic acid and its ethyl ester close to 1 US \$/ 1 kg.

It is also worth mentioning that tests performed in accordance with the BTCA method were successful with the following raw biomass materials: wood chips (hardwood = birch; softwood = pine, spruce and fir) and (wheat and rice) straws. Differences in the biomass conversion performance were consistent with the differences in the intrinsic properties of the raw materials.

3 Fenton's reagent for lignin depolymerization in BTCA char

By-products released by lignin and the structural degradation of such component during the BTCA pre-treatment phase, e.g. formic acid and methanol, constitute a clear evidence that Fenton's reagent in acidic ethanol medium heated at a temperature close to the boiling point of H₂O₂ has some capability of lignin depolymerization, probably by cleavage of some ether bonds, mostly β-O-4 bonds.

Carboxylic and dicarboxylic acids (in ester forms) and alkyl aromatics, analogous to those found in reference [6], can be produced, in quite high yields in some cases. However, the conversion trends are extremely difficult to follow, suggesting a great complexity of the chemical interactions occurring in the reaction medium. Our method differs from the five types of lignin depolymerization treatment as reviewed by Wang et al [7] (base-catalyzed, acid-catalyzed, metallic catalyzed, ionic liquids-assisted, supercritical fluids assisted) since in our case, free radicals and electrophilic ions might be the main actors for conversion. Nevertheless, a new conversion technique has been devised that consists of submitting the lignin char, being recovered from the BTCA process, to a sequence of depolymerizing operations in controlled mode (in cascade): this procedure results finally in liquid product yields well exceeding 70 %. Products include C1-C6 carboxylic acids (and some dicarboxylic acids such as succinic and adipic acids), obviously in ethyl ester forms, and alkyl-aromatics within the kerosene range, i.e. “>C9” (and some dimers).

Our preferential product spectrum for such advanced BTCA process includes levulinic acid and its ethyl ester, ethyl esters of C1-C3 carboxylic acids, esters of dicarboxylic acids such as succinic and adipic acids and some other compounds. Such product distribution (and limitation) that may prevent future technical problems related to products separation, can be achieved by a judicious choice of lignin depolymerization parameters, to be used with the “cascade” procedure.

4 Conclusion

In the BTCA process, by using Fenton’s reagent to “disrupt-open” the protective lignin layer of lignocellulosic biomass material in the pre-treatment phase, and then, by adding a “water-ethanol” mixture, in a well determined ratio, to the acid conversion slurry, levulinic acid and its ethyl ester are produced, with ethyl formate and ethyl acetate as main by-products. The production of the unwanted by-product diethyl ether is considerably reduced. Such procedure allows the complete recovery of formic and acetic acids as their corresponding ethyl esters, both having relatively high commercial values. Moreover, the consumption of hydrogen peroxide is considerably reduced when compared with the previously developed one-pot technology (AC3B). With such overall process improvements, the production cost of levulinic acid and its ethyl ester has significantly decreased.

It is also shown that treating the BTCA char with Fenton’s reagent under moderate severity condition, may result in the production of liquid products such as carboxylic (& dicarboxylic) acids and alkyl-aromatics. In particular, alkyl aromatics can be used for tailoring new “green” bio-jet fuels.

All these compounds have quite high commercial values (some of them been mentioned in ref. [8]), so that the economics of the entire process can be greatly improved [9]. Finally, could the newly found technique of lignin depolymerization be applied to other types of lignin, a biomass-based refinery would be conceived as shown in Figure 3.

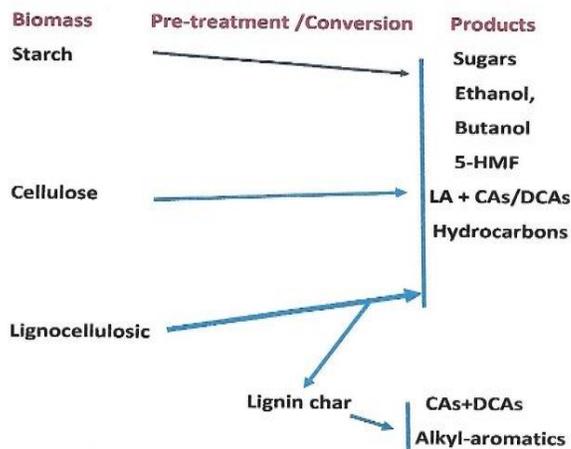


Figure 3: General scheme of a biomass-based refinery (5-HMF: 5-hydroxymethyl furfural; LA: levulinic acid; CAs+DCAs: carboxylic/dicarboxylic acids; Hydrocarbons: light olefins, aromatics, gasoline and others; alkyl-aromatics).

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