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# AC3B Technology for Direct Liquefaction of Lignocellulosic Biomass: New Concepts of Coupling and Decoupling of Catalytic/Chemical Reactions for Obtaining a Very High Overall Performance

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**Abstract** The acid-catalyzed conversion of lignocellulosic biomass (AC3B) process has been developed for the direct liquefaction of lignocellulosic biomass. In the original version, the main products, ethyl esters, are produced in acidic medium containing ethanol, using a one-pot conversion system. Our research strategy for obtaining a high overall performance is based on two general concepts: (a) coupling of catalytic/chemical reactions that lead to desired products and (b) decoupling of reactions that produce unwanted products, by decreasing the effectiveness of these reactions. Concept (a) is realized by using oxidizers (hydrogen peroxide and Fenton's reagent) that promote a higher production of carboxylic acids as main intermediates, while concept (b) contributes to a significant decrease of undesired formation of polymeric products. As result of these reaction coupling and decoupling, the overall yield of liquid products has been multiplied by a factor of 2.5 (from 27 to over 70 wt%). Not only the yields of products from cellulose and hemicellulose components experience considerable increases, but also the lignin component starts undergoing a noticeable conversion. Essentially, the AC3B process, in the most recent version, consumes ethanol that is partly used to produce liquid fuels and chemicals from lignocellulosic biomass. The other amount of feed ethanol is converted—via diethyl ether and over ZSM-5-based catalysts—into aromatics-rich gasoline and liquefied petroleum gas—grade hydrocarbons.

**Keywords** Bio-fuels · Bio-chemicals · Direct liquefaction · Lignocellulosic biomass · Coupling and decoupling of catalytic/chemical reactions · Oxidative cracking

## 1 Introduction

Energy consumption has increased steadily over the last decades as world population has grown and more countries have become industrialized (the so-called emerging countries such as China, Brazil and India) [1]. The reserves of fossil fuel, especially crude oil, are limited and will be depleted as the consumption rate will likely increase in the medium term. In addition, several environmental and political preoccupations have spurred interests in developing technology for the production of energy, fuels and chemicals from long-lasting or renewable sources.

Biomass (forest and agricultural residues, municipal wastes, by-products and wastes of the pulp and paper industry, perennial grasses, vegetal oils and oils from algae, etc.) is currently considered as good renewable sources of energy, transportation fuels and chemicals. In general, biomass contains cellulose, hemicellulose and lignin, the so-called lignocellulosic biomass materials [2].

The acid-catalyzed conversion of lignocellulosic biomass (AC3B) process is based on the use of diluted solutions of (liquid) mineral acids such as sulphuric acid [3]. Although there is a conventional method of conversion that consists of carrying out first the hydrolysis in aqueous medium of the biomass then the esterification of the resulting carboxylic acids with ethanol (SEQ or sequential method), the direct method (D) has been chosen because of its better energy efficiency [3]. In fact, by

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using ethanol as reactant and solvent (dilute solution of acid in ethanol) directly on the biomass material, ethyl esters are mainly obtained [3]. In addition, by connecting the reactor (a simple stirred tank reactor) with a dry-vacuum system that is capable of delivering very mild vacuum (down to 20 mmHg), various reaction products can be easily recovered in solution in ethanol after the conversion operation. Recovery and semi-separation of products and (unconverted) ethanol can be achieved with such mild vacuum-assisted distillation (MVAD) procedure whose evolution is controlled by a special computer program [3].

As expected, when lignocellulosic biomass is submitted to an acid-catalyzed conversion that goes beyond glucose, xylose or other sugars as needed intermediates for alcohol fermentation [4, 5], the following final products are obtained in the presence of ethanol [3]:

- From the hemicellulose component: ethyl formate, ethyl acetate and 2-furfural (and also some ethyl levulinate, depending on the content in glucomannans of this component).
- From the cellulose component: ethyl formate and ethyl levulinate (and some non- esterified levulinic acid).
- The lignin component is not converted.

Besides some water being released by the biomass degradation, diethyl ether (DEE) was produced in quite significant amount due to the dehydration of ethanol over the acid catalyst [3]. As mentioned earlier, the degradation of various components of the biomass is let to go beyond the various sugars normally being the main products or intermediates of the industry of sugars or alcohols (ethanol, butanol [6]). Actually, the conversion of each biomass component involves dozens of steps [4] during some of which, there are unwanted side-reactions that produce insoluble polymers and resins. These solids being collected together with unconverted lignin are called tars, char (lignin char) or humins (improperly).

It is worth noting that potential commercial uses of the main products of the AC3B process include the following [3, 14]:

- Ethyl levulinate: blend component in “low-smoke, low sulphur emission” diesel/biodiesel formulations.
- Ethyl formate: “safe” grain and fruit fumigant.
- DEE: intermediate for the production of hydrocarbons.

## 2 Our Research Strategy for Enhancing the Performance of the AC3B Process

Considering the results of our previous work [3], there are four things that are of great importance for our process:

1. The main products of the degradation of cellulose and hemicellulose are carboxylic acids that are rapidly converted into ethyl esters with ethanol present in the reaction medium. If we want to increase the yields of these esters, we have to favour the formation of carboxylic groups in various intermediate molecules formed during the degradation of cellulose and hemicellulose, i.e. to favour the oxidation of some key aldehyde-type or alcohol-type intermediates. Particularly, hydrogen peroxide can play the role of such oxidizer, because of its suggestive action in the pulp and paper industry as a bleaching reagent [7], its use for water treatment (oxidative photochemical degradation of organic pollutants) [8], as well as, its capability to promote oxidative cracking of precipitated hardwood lignin [9]. However, while this reaction can be quite efficient in alkaline medium, the reaction mechanism in acidic medium is not well evidenced [9]. Fenton-type reagents (hydrogen peroxide + Fe(II) ions) [10, 11] are much stronger oxidizers due to the formation of free hydroxyl or “secondary” organic radicals [10, 12]. This strategy to couple the de-polymerization effect of the acid (catalyst) with the action of an oxidizer (hydrogen peroxide) being activated by metallic ions (co-catalyst: Fe(II)), is similar to the strategy recently identified by a panel of experts (B. Shanks, A.Datye, R.Davis, M. Neurok and J. Dumesic) as functional coupling at the molecular scale [13].
2. During the hydrolysis-degradation of the cellulose and hemicellulose components of the biomass, very unwanted reactions occur that result in the formation of polymeric and resinous products. These insoluble products form with the unconverted lignin these famous tars whose commercial value is quite low: nevertheless, they can be used as solid fuel for the production plant, owing to their high heat value [14]. This time, our strategy is based on de-coupling of catalytic-chemical reactions: enhancing desired reactions on one side and decreasing unwanted reactions on the other side: this approach recalls the concept of “kinetic coupling” proposed by Boudart and Djega-Mariadassou [15] (actually, our approach would be a “kinetic de-coupling”). The desired reactions are those that produce commercially valuable liquid products from the biomass whereas the unwanted reactions are those that contribute to the build-up of the solid tars.
3. As pointed out in our previous work [3] and also in those of others researchers [16], DEE is produced in quite significant amounts. This highly volatile liquid is directly formed from ethanol in acidic medium and at relatively high temperatures. Thus, it is absolutely necessary to convert DEE further into other valuable

chemicals because DEE has a quite limited commercial usage (mainly as solvent).

4. Finally, in all these attempts to improve the performance of the process, the environmental aspects of the catalysts-chemicals used have to be seriously considered.

In fact, in order to apply in practice the two concepts of coupling and de-coupling of reactions to a truly "green" conversion of lignocellulosic materials, we have to choose for our process and from the very beginning of our investigations, only reactants-catalysts-solvents that are harmless to the environment.

## 3 Experimental

### 3.1 Materials and Chemicals

Residues of jack pine wood (chips) and paper pulp were dried overnight in oven at 210 °C. Ethanol (absolute, Aldrich), n-dodecane or n-decane (Aldrich), hydrogen peroxide (Aldrich, aqueous solution), Fe(II) sulfate (Aldrich, heptahydrate), sodium sulphite (Aldrich) and sulphuric acid were used without any further treatment.

Approximate compositions of the two raw materials used in this work are as follows:

- Jack pine wood residues: cellulose = 42 wt%, hemicellulose = 26 wt% and lignin = 31 wt%.
- Bleached paper pulp (Cascades, small pieces):cellulose = 78 wt% and hemicellulose = 16 wt% and 6 wt% as some organic and inorganic compounds.

### 3.2 Experimental Set-up

The experimental set-up comprises two sections: the reactor (stirred tank, 1 L of capacity) and a dry-vacuum device, Welch Model 2028, used for the MVAD of the liquid products: all this was already described in Ref. [3].

### 3.3 Testing Procedure

Conversion of the biomass materials was carried out in the reactor, in accordance with the method D as described in Ref. [3]. A water-cooling system was used to stabilize the reactor temperature and control the heating rate. In some runs, several heating steps were used.

Essentially, depending on how "dense" is the raw biomass materials (wood chips being much less dense than solid pieces of paper pulp or extrudates of wood residues), 80 g of raw biomass are added to a solution of: 180–240 g of ethanol + sulphuric acid (in ethanol solution) + $Fe^{2+}$ in sulphate form dissolved in water + Na sulphite in aqueous solution + and finally $H_2O_2$ (ca. 8–10 g in aqueous solution).

### 3.4 Extraction and Analysis of Products and Solvents

These operations were described in detail in Ref. [3]. Liquid products were analyzed with a gas chromatograph (Agilent Tech 7890A, Network GC System) equipped with a DB-Wax capillary column.

### 3.5 Conversion of DEE, a By-product of the AC3B Process

The experimental set-up, testing procedure and product analysis were identical to those described in Ref. [17]. The reactor was a tubular catalytic reactor heated at 300 °C. The weight hourly space velocity (W.H.S.V.) was ca. 1.5–3.0 $h^{-1}$. In particular, the feed was DEE or a mixture of DEE, light ethyl esters and methanol, all in solution in ethanol, as collected from a biomass conversion run. Coke deposition is normally determined by weighing (spent catalyst vs. its decoked form), frequently controlled by thermal gravimetric analysis (TGA).

### 3.6 Configuration of the Entire Set-up

Figure 1 shows the entire set up that comprises the batch reactor used for the conversion of the lignocellulosic biomass, the MVAD system for the recovery of liquid products and the tubular catalytic reactor for the conversion of DEE or mixtures of DEE with light products obtained from the biomass, into hydrocarbons.

### 3.7 Product Yields (Definitions)

#### *3.7.1 For the Biomass Conversion*

The yield of these products is defined as follows:

Yield of product (i), expressed in wt% = weight of product (i), expressed in g, obtained per 100 g of (dry) raw biomass material (wood chips or paper pulp). The total liquid products of biomass conversion are called reaction products (RP).

Although DEE is not produced from the biomass, its yield is defined in the same manner, i.e. weight of DEE produced (g) obtained per 100 g of (dry) raw biomass material (conversion level (Tables 1, 2, 3): just to have an idea of the DEE production for each run).

#### *3.7.2 For the Conversion of DEE or Mixtures of DEE and Other Light Products from Biomass*

Yield of hydrocarbon (i), expressed in wt% = weight of hydrocarbon (i), expressed in g, obtained per 100 g of DEE (or mixture).

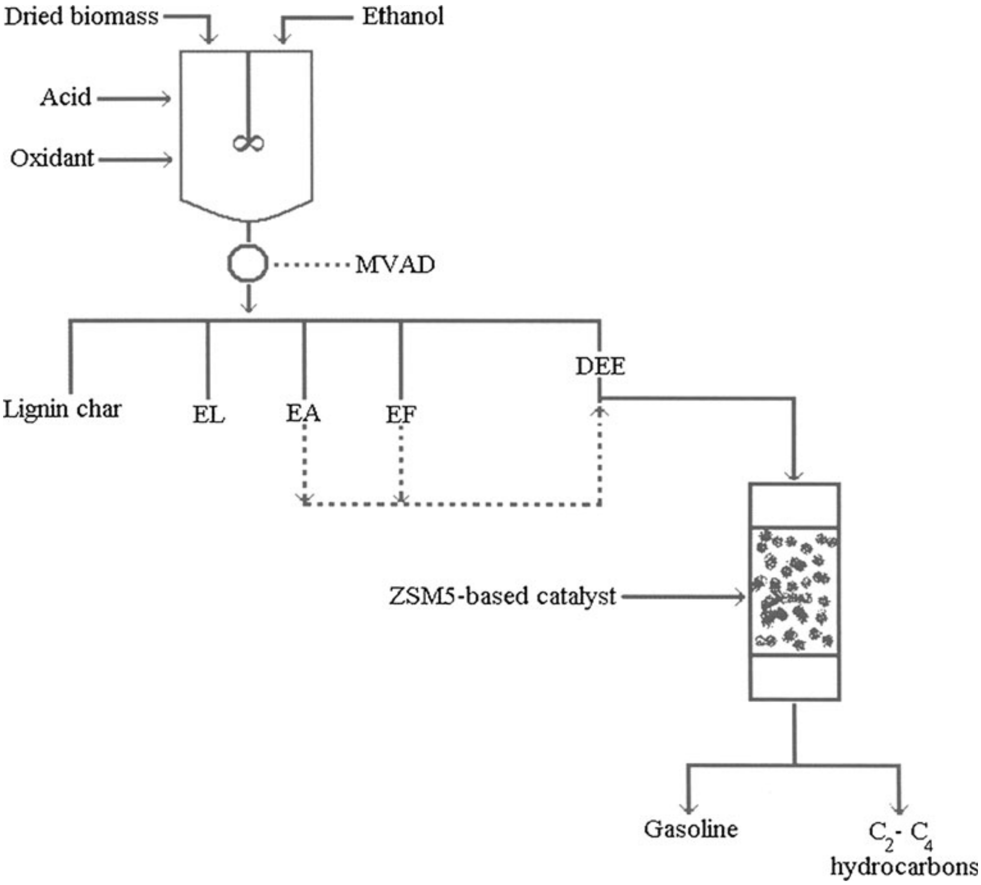

**Fig. 1** Schematic representation of the entire system of the AC3B process for the direct liquefaction of lignocellulosic biomass

**Table 1** Improved yields from ligno-cellulosic (pine wood chips) with the use of hydrogen peroxide

| Example number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Method | SEQ | D | D | D | D |
| Acid concentration (wt%) | 2.1 | 2.1 | 2.6 | 2.6 | 2.6 |
| $H_2O_2$ concentration (wt%) | NO | NO | 3.6 | 3.6 | 5.4 |
| Reaction temperature (°C) | 192/145 | 190 | 157 | 140/157 | 140/157 |
| Product yields (wt%) | | | | | |
| Light ethyl esters | 9.2 | 8.0 | 19.3 | 22.5 | 23.3 |
| 2-Furfural | 1.1 | 0.9 | 0.0 | 0.0 | 0.4 |
| Methanol | 0.0 | 0.0 | 1.5 | 1.2 | 1.7 |
| Ethyl levulinate + levulinic acid | 17.2 | 18.0 | 14.6 | 21.3 | 19.9 |
| RP (liquid products from biomass) | 27.5 | 26.9 | 35.4 | 45.0 | 45.3 |
| DEE (conv. level.) | 2.0 | 64.3 | 46.2 | 47.8 | 45.5 |

## 4 Results and Discussion

In our previous work [3], it was mentioned that the direct conversion procedure, called method D, was more favourable than the SEQ in terms of energy consumption. Method SEQ consisted of an acid-hydrolysis followed by an advanced water removal using the MVAD system, and finally ended with an esterification with ethanol over the same acid catalyst. With method D, the "hydrolysis" and esterification were simultaneously carried out with sulfuric acid in dilute ethanol solution. The convenience of method D was compensated by a significant production of DEE directly from ethanol, because the biomass conversion occurred at quite elevated temperature (Table 1, examples 1 and 2). Method D was finally chosen because the problem of DEE was solved with its quite easy conversion over ZSM-5 zeolite into commercially valuable hydrocarbons.

As pointed out in Sect. 2 regarding our research strategy, it is in principle possible to enhance the yields of wanted products by harnessing (coupling) the catalytic/chemical reactions that have individually positive effects on these yields. In our case, the wanted products are carboxylic

**Table 2** Effect of Fenton's reagent (Fe(II) + $H_2O_2$) on the product yields in the conversion of ligno-cellulosic biomass

| Example number | 6 | 7 | 8 | 9 | 10[a] |
|---|---|---|---|---|---|
| $[Fe(II)/H_2O_2] \times 10^{-2}$(g/g) | 0.0 | 0.4 | 0.8 | 1.6 | 0.8 |
| Product yields (wt%) | | | | | |
| Light ethyl esters | 22.2 | 25.6 | 28.3 | 27.1 | 26.3 |
| 2-Furfural | 0.3 | 0.5 | 0.0 | 0.3 | 2.3 |
| Methanol | 1.6 | 1.6 | 1.4 | 1.6 | 0.0 |
| Ethyl levulinate + levulinic acid | 21.8 | 27.3 | 28.3 | 27.5 | 43.2 |
| RP (liquid products from biomass) | 45.9 | 55.0 | 58.0 | 56.5 | 71.8 |
| DEE (conv.level) | 51.6 | 47.1 | 54.4 | 60.7 | 49.6 |

Concentration of acid = 2.6 wt%, $H_2O_2$ = 4.4 wt%, Heating steps = 140/157 °C

[a] run carried out with paper pulp

**Table 3** Inhibiting the formation of solid polymers with sodium sulphite

| Example number | 11 | 12 | 13 |
|---|---|---|---|
| Na sulphite (wt%) | 0.4 | 0.5 | 0.7 |
| Acid concentration (wt%) | 2.6 | 2.8 | 2.8 |
| Product yield (wt%) | | | |
| Light ethyl esters | 25.7 | 26.5 | 22.9 |
| 2-Furfural | 0.7 | 1.4 | 1.0 |
| Methanol | 1.6 | 1.5 | 1.5 |
| Ethyl levulinate + levulinic acid | 34.0 | 41.0 | 40.2 |
| RP (liquid products from biomass) | 62.0 | 70.4 | 65.6 |
| DEE (conv.level) | 60.5 | 53.1 | 47.8 |
| Washed lignin char (wt%) | 48 | 43 | 46 |

*Reaction conditions*: Temperature = 140 °C for 60 min and 157 °C for 240 min; $H_2O_2$ = 3.6 wt%, $[Fe(II)/H_2O_2] \times 10^{-2}$ (g/g) = 0.8

acids (i.e. precursors of the corresponding esters), so that the main effect that we have to channel into the same direction is oxidation (of carbohydrates and their reaction intermediates). This has been achieved in two steps, as depicted in the next Sects. 4.1 and 4.2.

Section 4.3 will show how decoupling of reactions, by retarding the reactions (i.e. lowering the rates of formation) that produce unwanted solid products, can be achieved. These solid products, polymers and resins, together with unconverted lignin, form the so-called lignin char or tars. Decreasing the production of these reactions also means increasing that of the reactions that lead to desired carboxylic acids.

Section 4.4 will show how DEE, the most non-desirable product whose production is very difficult to suppress or to significantly decrease during the biomass conversion, can be converted into highly valuable products.

### 4.1 Coupling of reactions: improved yields of liquid products from biomass with the use of hydrogen peroxide

In Sect. 2, our strategy to improve the yields of the ethyl esters of various carboxylic acids consists of using an oxidizer to increase the production of these acids, and consequently the corresponding esters. The carboxylic acids that are normally produced by acid-catalyzed conversion of the cellulose and hemicellulose components of the biomass [4] are: formic acid, acetic acid (note: the expected glycolic acid is formed in quite negligible amount) and levulinic acid. Thus, the final product esters of our process are: ethyl formate, ethyl acetate and ethyl levulinate [3].

The more active reaction medium that contains hydrogen peroxide, allows us to operate at much lower temperature, as shown in Table 1 (example 3 vs. examples 1 and 2). The yield of light ethyl esters (ethyl formate + ethyl acetate) increases steadily with the presence of the oxidizer (Table 1, example 3), suggesting that at 157 °C, hydrogen peroxide in acid medium is rapidly decomposed in oxygen (and water), so that only the light carboxylic acids produced from the easily hydrolysable hemicellulose are affected by the reactive electrophilic species $OH^+$ produced from $H_2O_2$ and $H^+$, as hypothesised by Xiang and Lee [9].

If a heating step at 140 °C is incorporated and this precedes the main heating step at 157 °C, surprisingly the yield of levulinic acid is significantly increased. In fact, the production of its ester form (ethyl levulinate) experiences an increase of more than 45 % (example 4, Table 1). Our interpretation is that at lower temperature, hydrogen peroxide has all the time to oxidize more the lignin component, freeing more the cellulose component with as immediate result a higher yield of 5-Hydroxymethyl-2-furaldehyde (5-HMF) [4]. It is to note that the 5-HMF later splits into levulinic acid and formic acid at higher temperature (157 °C in our case).

The case of methanol production is quite intriguing. Table 1 shows that methanol is a biomass conversion product found in examples 3 and 4, while it is absent in examples 1 and 2. Examples 3 and 4 report the results obtained with the use of hydrogen peroxide that is known to be capable of (partially) de-lignifying woody materials. Such pre-treatment operation (also called oxidative delignification [18]) is used to expose better the cellulose (and also the hemicellulose) component to the further hydrolytic action of acid or enzymes. Oxidative decomposition of lignin yields light carboxylic acids such as formic acid and acetic acid in substantial amounts [9, 19]. At higher conversion temperatures, succinic acid is the predominant product [19]. Anyway, in the proposed reaction mechanism of the oxidative degradation of lignin [19], methanol is one of the by-products. Another experimental evidence that methanol comes from the oxidative degradation of lignin, is that in all our runs involving paper pulp and being carried out with hydrogen peroxide, absolutely no methanol is produced because paper pulp does not contain any lignin [20] (example 10 of Table 2).

In terms of hydrogen peroxide concentration, it appears that over an oxidizer content of 3.6 wt% in the reaction medium, the various product yields have reached a certain plateau (examples 4 and 5, Table 1). Thus, such low content of hydrogen peroxide (ca. 3 wt%) is not an excessive economic burden for the entire process. After the reaction, it is obvious that hydrogen peroxide is transformed into oxygen that can be safely vented out. It is to note that no significant amount of carbon oxides is detected in all our runs, suggesting that the oxidative cracking of various components of the biomass is quite controlled.

Finally, Table 1 shows that in such oxidative acidic conversion medium, 2-furfural can be converted into formic acid (thus in ethyl formate with ethanol), as evidenced by the disappearance of 2-furfural in the product spectra of examples 3 and 4: this has been confirmed by our research team that found that pure 2-furfural and pure xylose when heated in a medium containing sulphuric acid, hydrogen peroxide and ethanol, are at least partially converted into ethyl formate [20].

### 4.2 Coupling of Reactions: Improved Yields of Liquid Products from Biomass With the Use of Fenton-Type Reagents

The most known Fenton-type reagent is the combination of hydrogen peroxide and Fe(II) ions [10–12]. Because of its high oxidative strength, the Fenton reagent "$H_2O_2$–Fe(II)" can be used in almost the same applications as hydrogen peroxide, such as to degrade polycyclic aromatics in aged oil samples from various contaminated sites [21] and other organic pollutants [8], to treat landfill leachate (complex wastewater) [22], to improve dewaterability, reduce pathogen levels and significantly reduce levels of certain metals (Cu, Zn, Cd, Ni) in raw primary and activated sewage sludge [23].

When Fe(II) sulphate is added to the reaction medium that already contains hydrogen peroxide, very significantly improved product yields are obtained (Table 2). It is to note that the concentration of Fe(II) ions used is extremely low (Table 2), in the order of magnitude of 200–300 ppm as concentration in the reaction medium, so that Fe(II) ions really play the role of catalyst for hydrogen peroxide. Nevertheless, at such extremely low concentration and because Fe ions do not represent any environmental problem, its presence in the solid tar does not disturb much the use of this materials as fuel to produce electricity for the production plant.

Data of examples 6 through 9 show that Fe(II) reaches the maximum of efficiency at the concentration of example 8 (i.e. ca. 250 ppm in the reaction + medium) and additional amount of such ion does not increase the total product yield RP.

On the other hand, the total product yield (RP) obtained with bleached paper pulp (example 10 of Table 2) is much higher than that obtained with the pine wood chips, because paper pulp has a much larger content in cellulose and does not contain any hard-to-be-converted lignin (Sect. 3.1). As already mentioned in Sect. 4.1, no methanol is produced when the feed is paper pulp.

### 4.3 Decoupling of Reactions: Decreasing the Rate of Formation of Solid Polymers and Resins

Review of scientific and patent literature shows various methods that are claimed to retard or eliminate the formation of solid polymeric species from assumed reaction intermediates of the numerous and multi-branched degradation pathways of lignocellulosic materials. Although the exact nature of these polymeric substances is not well known [14], it is assumed that insoluble humins (tars or lignin char) are formed from glucose and 5-HMF, and from xylose and 2-furfural, 5-HMF and 2-furfural being the main intermediates of the degradation of cellulose and hemicellulose, respectively. In particular, by using the same conditions as in example 4 of Table 1 (acidic-oxidative reaction medium), 2-furfural is partially decomposed in formic acid (ethyl formate because of the presence of ethanol) and insoluble char (more than 60 wt%) [20]. The same behaviour (i.e. significant formation of char) is observed with xylose, and also with glucose and 5-HMF, confirming thus the previously made assumptions [20].

Several inhibitors of 2-furfural polymerization such as arylendiamines [24] or alkyl thiocyanate [25], have been proposed. However, because these inhibitors may raise problems of toxicity and/or violent reactions (explosion) with the reactants/catalysts used in our process, they are all discarded. Sodium sulphite, that was (timidly) mentioned in the Biofine process [14, 26] and used in the process for the preparation of flame-retardant cellulosic materials [27], has been tested very successfully by our research group (Table 3). It can be seen that the weight of washed lignin char is much lower than 50 wt%, meaning that more than

**Table 4** Conversion of DEE over HZSM-5 zeolite catalyst

| Example number | 14 | 15 | 16 | 17 |
|---|---|---|---|---|
| WHSV ($h^{-1}$) | 3.0 | 1.5 | 1.5 | 1.5 |
| $H_2O$/DEE weight ratio | 0 | 0 | 0.5 | 1.0 |
| Product yield (wt%) | | | | |
| Liquid hydrocarbons (BTX aromatics) | 54 (31) | 55 (28) | 56 (26) | 55 (22) |
| $C_2$–$C_4$ paraffins (LPG grade) | 37 | 40 | 35 | 27 |
| Methane | <0.01 | <0.01 | <0.01 | <0.01 |
| Light olefins and diolefins[a] | 7 | 32 | 7 | 17 |
| Total product yield (wt%) | >98 | >98 | >98 | >99 |
| Coke | 0.8 | 1.5 | 0.5 | <0.1 |

[a] Ethylene, Propylene, Butenes and Butadienes: 1/3 each type (approx)

half of the ligno-cellulosic material is converted into liquid products. Consequently, there is a general increase in the product yields (example 12 of Table 2 vs. example 8 of Table 2). Since the strongest increase occurs with ethyl levulinate, it is reasonable to say that sodium sulphite is affecting more the polymerization of 5-HMF (precursor of levulinic acid, thus ethyl levulinate) than that of other intermediates. This is an example of reaction (or "kinetic") decoupling: in fact, retarding the rate of polymerization of 5-HMF is equivalent to enhancing its rates of formation in the reaction medium and of its subsequent splitting into levulinic and formic acids.

For the moment, we do not know that is, exactly, the chemical or catalytic effect of the sodium sulphite (polymerization inhibition by sulphite species, Na ions that may alter the acidity of the reaction medium, or mixed effect). In addition, data of examples 11 through 13 show that there is some kind of saturation beyond a concentration of Na sulphite of 0.5 wt% in the reaction medium.

It is to note that the use of oxidizers like hydrogen peroxide or Fenton's reagent, in quite mild reaction conditions as used in this work, does not produce noticeable amounts of carbon oxides: such result thus affects positively the life cycle assessment of the process because the absence of greenhouse gas (GHG) emission during the biomass conversion is considered very favourably. All these results coincide with the belief that lignocellulose-based ethanol production is a net energy-producing process and shows significant reduction in GHG emission [1].

### 4.4 Catalytic Conversion of By-product DEE into Commercially Valuable Hydrocarbons

DEE is the reaction intermediate of the conversion of ethanol into hydrocarbons over ZSM-5-based catalysts [28]. Normally, if ethanol is used, the main reaction product is ethylene as in the bioethanol-to-ethylene process that was developed in the late 1970 in our laboratory [29–31]. However, by using suitable surface acidity (Si/Al ratio of 50 for the ZSM-5 zeolite) and appropriate reaction parameters (see the following paragraph), the reaction goes beyond the olefinic intermediates and follows the hydrocarbon pool mechanism as proposed for methanol [32] and also observed for ethanol [33].

In this work, DEE is sent to a tubular reactor heated at 300 °C. Other reaction conditions are: catalyst = HZSM-5 (Zeochem, 1/16" extrudates, Si/Al = 50, weight = 2 g); W.H.S.V. = 1.5–3 $h^{-1}$; duration of a run = 4 h). The catalytic results are reported in Table 4.

The results of Table 4 can be summarized as follows:

a) There is no production of methane that is not only a powerful GHG but also, not of a great commercial value as chemical or fuel.
b) Gasoline-grade liquid hydrocarbons are predominantly produced. The yield of BTX aromatics (benzene, toluene, xylenes) is quite high.
c) Liquefied petroleum gas (LPG) grade hydrocarbons are produced in very significant amounts.
d) The production of light olefins becomes significant only at W.H.S.V.
e) Dilution of the DEE feed with some water drastically reduces the coke deposition.

If the entire mixture of light products collected at the exit of the biomass conversion reactor (i.e. DEE + ethyl formate + ethyl acetate + methanol) is sent over the HZSM-5 zeolite catalyst, the conversion is also complete in similar reaction conditions. The gasoline-grade liquid hydrocarbons are still the predominant products. However, the yield of light olefins increases significantly and can be almost equal to that of the LPG-grade light paraffins.

## 5 Conclusion

### 5.1 Enhancing the Performance of the AC3B Process with the Concepts of Coupling and Decoupling of Catalytic-Chemical Reactions

Let us consider the variation of the total yield of RP (i.e. the liquid products obtained from biomass and partly from ethanol) as a consequence of various actions on the reaction medium (Fig. 2) :

(a) RP = 26.9 wt% (normal reaction conditions: example 2 of Table 1).
(b) RP = 35.4 wt% (use of $H_2O_2$: example 3 of Table 1)
(c) RP = 45.0 wt% ($H_2O_2$, additional delignification step, example 4 of Table 1)
(d) RP = 58.0 wt% (use of a Fenton-type reagent, example 8 of Table 2)
(e) RP = 70.4 wt% (use of Fenton-type reagent + polymerization inhibitor, example 12 of Table 3).

Thus, between (a) and (e), there has been an increase in the total product yield RP of almost 160 %, i.e. RP has been multiplied by a factor of 2.5.

## 5.2 Comparison of Our Data with Those of the Current Industrial Process (Biofine)

Biofine process produces levulinic acid, formic acid, 2-furfural and other minor products [14, 26]. It is claimed that C6-sugars (mostly from cellulose) and C5-sugars (mostly from hemicellulose) are converted up to 50 %. Lignin remains unconverted. Thus, if jack pine wood residues were used, the average yield of the products obtained with the Biofine technology would be less than 42 wt% (referred to biomass).

The AC3B technology is more advanced in terms of conversion degree (we produce esters of levulinic acid and of other carboxylic acids, rather than carboxylic acids). Taking into consideration the data of example 12 of Table 3, the average total yield of products from softwood pine residues used in our work is 57 wt%. In fact, in example 12, the estimated yield of levulinic acid LA (that results from splitting of 5-HMF into "LA + formic acid' mole/mole) from the actually produced levulinic acid and ethyl levulinate, corresponds to 100 % of the theoretical yield for cellulose component (see composition of pine chips in Sect. 3.1). On the other hand, the yield of conversion products from hemicellulose (2-furfural, ethyl acetate, ethyl formate and some ethyl levulinate, the latter being produced by the glucomannans [1]) is estimated to 60 wt% and that of lignin (products= methanol + some formic and acetic acid) to ca. 15 wt%.

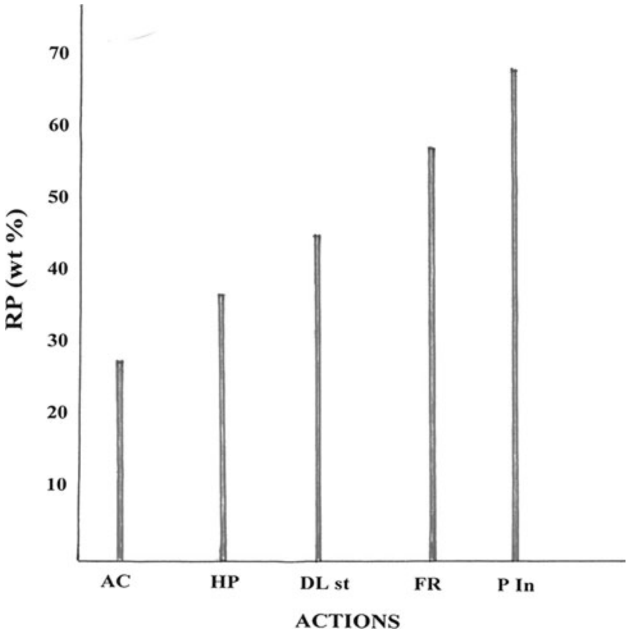

**Fig. 2** Sequence of actions that have significantly improved the total product yield (RP). *AC* Acidic medium, *HP*Addition of hydrogen peroxide, *DL-st* Use of a delignification step, *FR* Use of a Fenton-type reagent, *PIn* Use of a polymerization inhibitor

## 5.3 Mass Balance (Preliminary Study)

Let us consider example 12 of Table 3 that reports the best conversion performance of this work (pine wood chips).

The conversion of ethanol into 53.1 wt% of DEE corresponds to a consumption of 66 g of ethanol (bimolecular dehydration). The total yield of products from biomass is 70.4 wt%, corresponding to 16 g of ethanol consumed. Thus, the calculated weight of ethanol consumed is 82 g.

On the other hand, the total consumption of ethanol measured for this run is equal to 86 g: this gives a difference of 5 wt% that is quite acceptable as experimental error/loss.

## 5.4 Practical Realization of the Coupling/Decoupling Concepts

At first sight, these concepts are quite clear and direct: however, their practical application is very complex because we cannot pretend to have the cooperation of several catalytic and chemical reactions in one-pot reaction medium without perfectly knowing the actions of each species and its interactions with the others. In fact, in order not to have adverse effects due to these interactions, we have to make compromises using the operating parameters as main tools (temperature, duration of various heating steps, acidity, concentration, etc.), as well as, to imagine a precise sequence of addition of various solvents, reactants, catalysts, that have to contact the biomass material before and during the reaction.

## 5.5 The Problem of DEE

At the beginning of the AC3B process development, we were facing the serious problem of DEE. Numerous tests have been done in order to rehydrate DEE into ethanol or to convert it into dialkyl ethers using various alcohols as co-reactants. Finally, the most elegant way to get rid of DEE is to convert it into hydrocarbons. ZSM-5 zeolite appears to be the best catalyst because at relatively low temperature, this zeolite can yield aromatics-rich gasoline and LPG-grade hydrocarbons (and also, some light olefins). Although the conversion over acidic pentasil zeolites is almost complete, the conversion DEE-to-hydrocarbons occurs with a loss of one oxygen atom per molecule of DEE, resulting thus in a loss of weight of almost 20 %. It is to note that the yield of DEE in this work is equal to or lower than 60 wt% when referred to the weight of raw biomass material (examples 3–12 of Tables 1–3).

### 5.6 The (Current State of the) AC3B Process

- The biomass conversion is carried out in one reactor having a quite simple configuration (stirred tank reactor). Reaction products can be extracted (and purified) with the MVAD [3].
- By-product DEE is easily converted into valuable hydrocarbons (fuels and chemicals).
- Reactants, solvents and catalysts are all environmentally friendly.

Two production options are now available:

1. Bio-fuels: diesel-grade additive, gasoline and LPG + bio-chemicals: ethyl formate (fumigant) and ethyl acetate (large-usage organic solvent)
2. Bio-fuels: diesel-grade additive, gasoline and LPG + bio-chemicals: light olefins

The mild operating conditions used in the AC3B process (relatively low temperature and pressure), its overall conversion efficiency and its "green" character are key factors of advantage when it has to be compared with other processes of direct liquefaction of biomass [34].

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## References

1. Cheng JJ (2010) In: Cheng J (ed) Biomass to renewable energy processes. CRC Press, Boca Raton
2. Keshwani DR (2010) In: Cheng J (ed) Biomass to renewable energy processes. CRC Press, Boca Raton, p 7
3. Le Van Mao R, Zhao Q, Dima G, Petraccone D (2011) Catal Lett 141:271
4. Girisuta B, Janssen LPBM, Heeres HJ (2006) Chem Eng Res Des 84:339
5. Huber GW, Iborra S, Corma A (2006) Chem Rev 106:4044
6. Qureshi N, Blaschek HP (2010) In: Vertes AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to Biofuels: Strategies for Global Industries. Wiley, U.K, p 347
7. Andrews DH, Singh RP (1979) In: Singh RP (ed) The Bleaching of Pulp, 3rd edn. Tappi Press, Atlanta, p 211
8. Legrini O, Oliveros E, Braun AM (1993) Chem Rev 93:671
9. Xiang Q, Lee YY (2000) Appl Biochem Biotechnol 154:84–86
10. Merz JH, Waters WA (1949) J Chem Soc, S15; and references therein
11. Mae K, Hasegawa I, Sakai N, Miura K (2000) Energy Fuels 14:1212
12. Czapski G, Samuni A, Meisel D (1971) J Phys Chem 75:3271
13. Simonetti DA, Dumesic JA (2009) Catal Rev 51:441
14. Hayes DJ, Fitzpatrick S, Hayes MHB, Ross RH (2006) In: Kamm B, Gruber PR, Kamm M (eds) Biorefineries—industrial processes and products, vol 1. Wiley–VCH, Weinheim, p 139
15. Boudart M, Djega-Mariadassou G (1994) Catal Lett 29:7
16. Mascal M, Nikitin EB (2010) ChemSusChem 3:1349
17. Yan HT, Le Van Mao R (2011) Catal Lett 141:691
18. Kumar P, Barrett DM, Delwiche MJ, Stroeve P (2009) Ind Eng Chem Res 48:3713
19. Hasegawa I, Inoue Y, Muranaka Y, Yasukawa T, Mae K (2011) Energy Fuels 25:791
20. Le Van Mao R, Petraccone D, A Muntasar (Nov. 2011–Feb. 2012), Concordia University, unpublished data
21. Jonsson S, Persson Y, Frankki S, Bavel BV, Lundstedt S, Haglund P, Tysklind M (2007) J Harzard Mater 149:86
22. Wu Y, Zhou S, Qin F, Ye X, Zheng K (2010) J Harzard Mater 180:456
23. Andrews J, Asaadi M, Clarke B, Ouki S, Zagdaa Y (2006) J Residuals Sci Technol 3:137
24. Ghazi D (1994) US Patent 5,332,842
25. Sherwood CS (1956) US Patent 2,741,579
26. Fitzpatrick SW (1990) US Patent 4,897,497
27. Wagner GM, Hoch PE (1963) US Patent 3,101,278
28. Nguyen TM, Le Van Mao R (1990) Appl Catal 58:119
29. Le Van Mao R, Nguyen TM, McLaughlin GP (1889) Appl Catal 48:265
30. Le Van Mao R, Ly D, Yao J (1992) In: Albright LF, Crynes BL, Nowak S (eds) Novel production methods for ethylene, light hydrocarbons and aromatics, Chem ind 46. M Dekker, New York
31. Le Van Mao R, Dao LH, US Patent 4,698,452 (6 Oct. 1987)
32. Dahl IM, Kolboe S (1996) J Catal 161:304
33. Muntasar A, Le Van Mao R, Yan HT (2010) Ind Eng Chem Res 49:3611
34. Behrendt F, Neubauer Y, Oevermann M, Wilmes B, Zobel N (2008) Chem Eng Technol 31:667