# A New Technology for Utilization of Biomass Hydrolysis Residual Humins for Acetic Acid Production

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Humins are a major byproduct formed from acid-catalyzed biomass hydrolysis and are usually considered as a low-value material. In this work, humins were completely degraded by a two-step technology, involving alkaline-catalytic hydrothermal treatment followed by wet oxidation. Using this technology, humins were converted to value-added acetic acid for first time. The highest acetic acid yield of 25.6% on a carbon basis or 37.2% on a mass basis was obtained with a purity of 46.2% based on the organic carbon in the aqueous product. This high-efficiency recovery of acetic acid is a new method for the effective utilization of humins, which is an important finding for biorefineries.

*Keywords: Humins; Acetic acid; Wet oxidation; Hydrothermal treatment; Biomass; Levulinic acid*

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## INTRODUCTION

Acid-catalyzed conversion of the cellulose fraction of biomass to platform chemicals such as levulinic acid and 5-hydroxymethylfurfural has attracted great attention in recent years (Yang *et al.* 2013; Rackemann *et al.* 2014; Fu *et al.* 2015). A well-known example is the commercial-scale production of levulinic acid through the Biofine process (Kamm *et al.* 2006). However, humins, a carbonaceous, heterogeneous, polydisperse material, are unavoidably formed during the platform chemical production (Galletti *et al.* 2012; van Zandvoort *et al.* 2013). In the production of levulinic acid from cellulose hydrothermal conversion, humins formation based on carbon reached even as high as 30% to 60% (Weingarten *et al.* 2012). Humins are a low-value material but a major by-product, which decreases the utilization efficiency of cellulosic feed and thereby decreases the economic viability of biorefineries. This may be ameliorated by converting humins to value-added chemicals, although few efficient methods have been reported. One problem may be due to humins's macromolecular polymer structure, which resists solubility in common solvents.

Wet oxidation is a promising technology that is capable of decomposing macromolecular organic materials to useful low-molecular weight products (Baroutian *et al.* 2015). Acetic acid is a useful and widely applied chemical, which is stable and highly recoverable from wet oxidation of organic materials. As shown in Table 1, wet oxidation has been used for acetic acid production from various materials, including conventional biomass, municipal bio-solids, and sewage sludge. Hence, wet oxidation may be a potential method to convert humins to value-added low-molecular weight chemicals such as acetic acid. However, little work in this area has been reported. The wet oxidation efficiency may be limited because humins are insoluble in water, which restricts the mass transfer of the oxidation. Hydrothermal alkaline catalytic treatment has been applied for the dissolution and decomposition of water-insoluble macromolecular polymers (*e.g.*, lignin) (Kang *et al.* 2013). This technology has also been reported to be useful in the dissolution and degradation of humins (van Zandvoort *et al.* 2015), which may be beneficial for wet oxidation. Therefore, an original two-step technology involving alkaline catalytic hydrothermal treatment followed by wet oxidation was conducted in this work. The objective was to improve the degradation efficiency of humins and obtain a high yield of acetic acid.

**Table 1.** Acetic Acid Production from Wet Oxidation of Various Organic Materials

| Feedstocks | Wet oxidation conditions | Acetic acid yield on carbon basis | Acetic acid yield on mass basis | References |
|---|---|---|---|---|
| Rice hulls, | Two-step reactions (the first step: 300 °C, 1 to 2 min, 0% of $O_2$; the second step: 300 °C, 1 min, 70% of $O_2$) | 21.7% | - | Jin *et al.* 2007 |
| Cellulose, | | 16.3% | - | |
| Starch | | 17.5% | - | |
| Municipal bio-solids | Two-stage process (hydrolysis at 140 °C followed by wet oxidation at 220 °C) | 12% | - | Aggrey *et al.* 2012 |
| Rice hulls, starch | 300-320 °C, 2 to 3 min, oxygen supply of 70 to 100%, 100 to 30 MPa | 12% | - | Zhou *et al.* 2006 |
| Woods (pine, oak) | 171 to 227 °C, 30 min, 240 to 480 psi of oxygen pressure | - | 14% | McGinnis *et al.* 1983 |
| Black liquor | 170 and 230 °C, Fe/AC used as catalyst, the amount of $H_2O_2$ is equal to 1 wt% of black liquor | - | 6% | Muddassar *et al.* 2015 |
| Sewage sludge | 220 °C, 5 h (2 h for heating reactor), sufficient $O_2$ | - | 20.2% | Andrews *et al.* 2015 |
| Humins | Two steps, oxidant ($H_2O_2$) content was 75% of the initial COD | 25.6% | 37.2% | This work |

## EXPERIMENTAL

### Materials

D-(+)-Glucose (99%) and levulinic acid (LA, 98%) were obtained from J&K Chemical (Beijing, China). Acetic acid (99%), hydrogen peroxide ($H_2O_2$, 30%), and sulfuric acid ($H_2SO_4$, 98%) were obtained from Xiya Reagent (Chengdu, China).

### Reaction Conditions

All reactions were conducted in Teflon® reactors with 25 mL Teflon® containers and stainless steel cylinders. The Teflon® containers were sealed in stainless steel cylinders and heated in an air-circulated oven to a pre-set temperature. The reactor temperature reached the pre-set temperatures (± 2 °C) with a heating time of approximately 60 min. The holding time started after 60 min of heating and was recorded thereafter. After the reaction, the reactors were quickly cooled down under tap water.

## Recovery of Humins

Glucose (200 g/L) was used for levulinic acid production at 170 °C with a holding time of 6 h with 0.05 M $H_2SO_4$. The solid humins were collected through vacuum filtration and washed by excessive water, followed by drying at 100 °C.

## Alkaline Hydrothermal Treatment

For a typical alkaline catalytic hydrothermal treatment reaction, humins were reacted in a NaOH solution (0.5 M) at 180 °C for 12 h, with a ratio of 1 g of humins per 80 mL of NaOH solution. After the reaction, the humins-derived solution was acidified by $H_2SO_4$ to a pH of 1 to 2 to precipitate the solid residues. The humins conversion ratio here is defined as:

$$\frac{\text{humins weight - solid residue weight}}{\text{humins weight}} \times 100\% \qquad (1)$$

## Wet Oxidation

The wet oxidation process involved direct wet oxidation and two-step wet oxidation (TSWO), with $H_2O_2$ as the oxidant. The concentration of the oxidant was evaluated by the percentage of the initial chemical oxygen demand (COD) of humins samples, and the oxidant addition percentage ranged from 0 to 85%. For the initial COD measurement, a pre-weighted humins were firstly treated in the typical alkaline catalytic hydrothermal conditions, forming a homogeneous solution. The homogeneous solution was cooled down to room temperature and then used for COD analysis, with a 5B-3C type rapid COD analyzer (Lanzhou Lianhua Environment Protection Technology Co., Ltd., China). The obtained COD value was labeled as initial COD of the pre-weighted humins. Direct wet oxidation was conducted at 180 °C for 12 h by adding humins followed by $H_2O_2$ into water (or 0.5 M NaOH solution) before reaction. For TSWO, the humins were subjected to the typical alkaline-catalytic hydrothermal treatment as the first step. In the second step, the hydrothermally treated humins solutions were mixed with $H_2O_2$ for wet oxidation at 150 $^{o}$C for 1 h of holding time, followed by acidizing the aqueous solutions to pH=1-2. After these reactions, the aqueous products were diluted by water and kept for analysis.

## Analysis

The water-diluted liquid solutions after wet oxidation were analyzed using high-performance liquid chromatography (HPLC, Essentla SIL-16, Shimadzu, Japan) with a C18 column. The column was kept at 30 °C and eluted with deionized water-methanol solution containing 0.1% phosphoric acid at 0.6 mL/min. The volume ratio of methanol to water was 20 to 80.

The products from aqueous solution were extracted by methylene chloride and analyzed by gas chromatography mass spectrometer (GCMS) with an Agilent J&W DB-624 column by Shimadzu QP 2010 Plus system (Japan). The temperature of the injector was set at 250 °C. The column temperature program was 50 °C (held for 2 min) and ramped up to 260 °C (10 °C/min, held for 5 min). The total organic carbon (TOC) was measured by a TOC analyzer with a TOC-V CPH/CPN analyzer (TOC-V CPH/CPN, Shimadzu, Japan).

## RESULTS AND DISCUSSION

### Alkaline Catalytic Hydrothermal Treatment

The humins obtained were a black solid (Fig. 1A), with a crude chemical formula of $CH_{0.93}O_{0.48}$ based on elemental analysis. The humins were probably formed by acid catalytic dehydration of glucose $(CH_2O)_6$, as the lost molar ratio of H to O is 2.06 (equal to the ratio [(2 – 0.93)/(1 – 0.48)]) from glucose to humins, which is close to the H to O molar ratio of water ($H_2O$). In contrast to acid catalytic dehydration for the humins formation, alkaline catalytic hydrothermal treatment showed good effects on the dissolution of humins. After the hydrothermal treatment (0.5 M NaOH, 180 °C for 12 h), all the humins were converted into a black homogeneous solution (Fig. 1B). The dissolution of humins may be related to structural changes, and one change was monitored by FT-IR analysis. The relative intensity of the peak at 1025 $cm^{-1}$ for humins obviously decreased after the hydrothermal treatment (Fig. 2), which could be attributed to the breakage of ether bonds in humins. Hydroxyl groups are usually formed by the cleavage of the ether bonds, and the cleavage of the ether bonds in the NaOH solution indicates the formation of hydrophilic sodium salts (Roberts *et al.* 2011). Besides, the cleavage of the ether bond is conducive to the reduction of the molecular weight of humins. It was considered that the reduction of molecular weight and formation of polar functional groups were the reasons for the dissolution of humins (van Zandvoort *et al.* 2015). However, the humins conversion ratio resulting from direct alkaline catalytic hydrothermal treatment was only 33% for a holding time of 12 h (Fig. 3A). Only approximately 24% of humins carbon was converted into water-soluble low-molecular weight compounds, which consisted of oxygen-containing compounds including cyclic compounds, organic acids, and alcohols (compounds 1 to 6 and 10 to 14 in Table 2). Without a doubt, the acetic acid yield at this condition was very low: 2.4% on a carbon basis or 3.5 wt% on a mass basis. Extension of reaction time can improve the conversion ratio, but a still low conversion ratio of 63% was found even for a reaction time of 36 h (Fig. 3A).

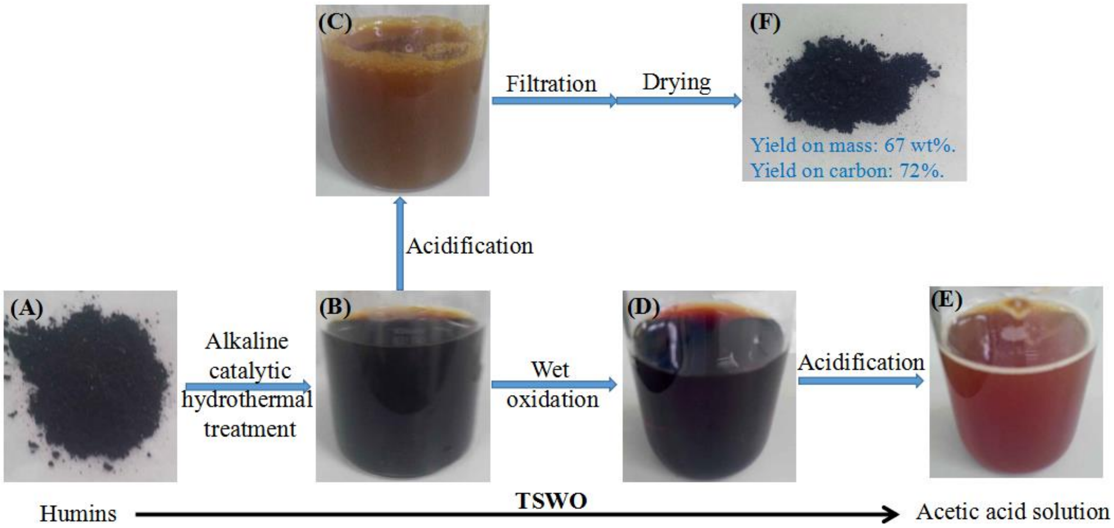

**Fig. 1.** A: humins; B: the aqueous solution obtained by humins alkaline catalytic hydrothermal treatment under typical reaction conditions; C: sample B with acidification; D: the aqueous solution obtained by wet oxidation of sample B; E: sample D with acidification; F: solid residues obtained from sample C

It seems that it was difficult for the hydrothermal alkaline catalytic treatment to decompose all the humins into low-molecular weight compounds. In other words, there may be some obstinate structure and/or bond in the humins that was stable during the direct alkaline catalytic treatment. Wet oxidation was therefore conducted for the degradation of humins.

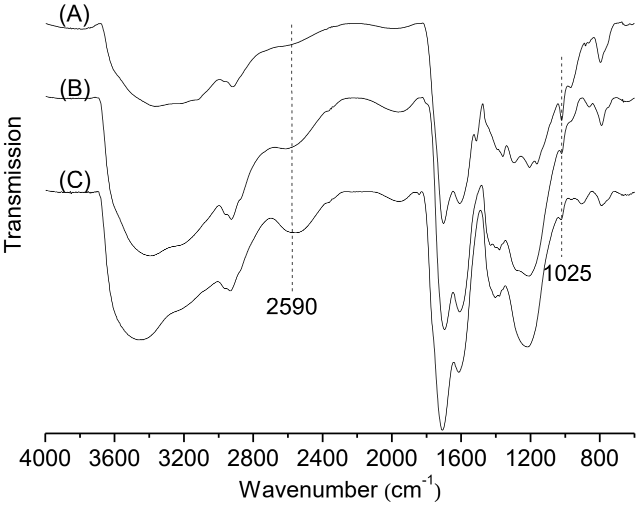

**Fig. 2.** FTIR spectra: (A) humins; (B) solid residue from humins alkaline catalytic hydrothermal conversion; (C) solid residue from TSWO technology with $H_2O_2$ addition equivalent to 30% of the initial COD.

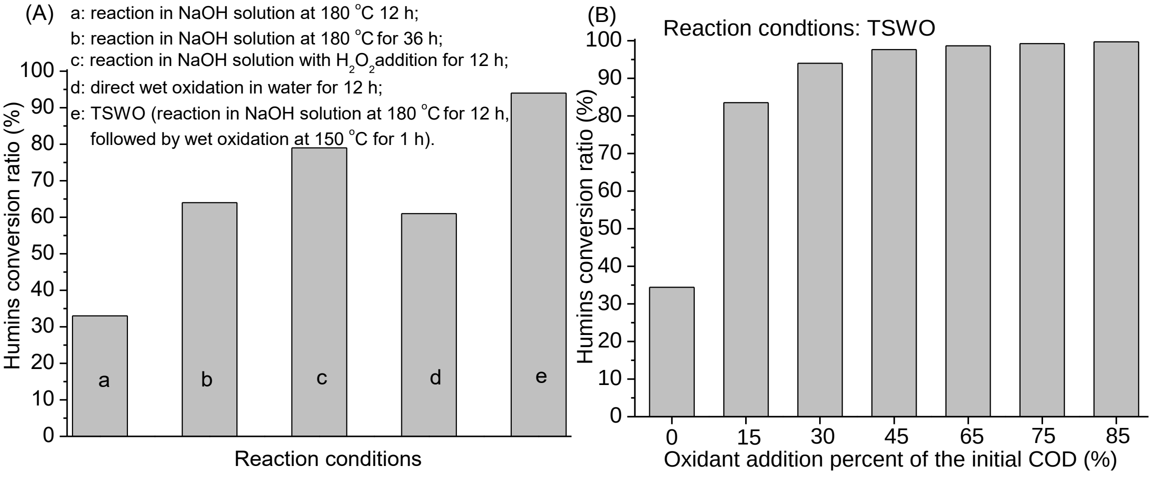

**Fig. 3.** The humins conversion ratio from various reactions. The $H_2O_2$ content of reactions c, d, and e in A was the same (equivalent to 30% of the initial COD).

## Wet Oxidation for Humins Degradation

As expected, the direct wet oxidation of humins in water led to decomposition of humins, resulting in a humins conversion ratio of 61% with the addition of $H_2O_2$ equivalent to 30% of the initial COD (d in Fig. 3A). Because the humins are insoluble in the routine hydrothermal condition, the conversion ratio of this heterogeneous reaction is quite low. This is because the inside part of humins would be protected from oxidation, while the surface part of humins might be over-reacted, with a limited oxidant content. The addition of $H_2O_2$ in the alkaline catalytic hydrothermal condition promoted the humins decomposition, with a conversion ratio that reached 78% under the same conditions (c in

Fig. 3A). Therefore, the presence of NaOH during the wet oxidation was good for humins degradation, because it could decrease the molecular weight of humins and lead to the formation of a homogeneous solution, which is beneficial to the mass transfer of oxidation reactions. However, the dissolution and degradation of humins in reaction conditions need a certain of reaction time, and longer reaction time results in much more low molecular compounds (van Zandvoort *et al.* 2015). On the other hand, $H_2O_2$ is unstable at elevated temperatures (Casson *et al.* 2012). At the reaction conditions in Fig. 3, or even at 150 $^oC$ for 1 h holding time in NaOH solution without humins addition, $H_2O_2$ was completely converted. In the simultaneous oxidation process (c in Fig. 3A), the alkali solution, $H_2O_2$ and humins were added into the reactor before heating. This means that the oxidation reaction occurred during the dissolution and degradation of humins. Therefore, the oxidation of humins includes two kind of reactions: homogeneous oxidation of the dissolved humins parts, and heterogeneous oxidation of the humins parts that did not dissolve. The second reaction is similar to the direct wet oxidation water (d in Fig. 3A), which resulted in a relative low conversion ratio.

It seems that wet oxidation conducted after the complete dissolution of humins can improve the degradation of humins. Therefore, the TSWO method, *i.e.*, alkaline-catalytic hydrothermal treatment followed by wet oxidation reaction, was conducted. For this TSWO method, the humins are completely dissolved in the alkaline solution, forming a homogeneous oxidation before the $H_2O_2$ addition. The homogeneous reaction promotes the contact of humins and $H_2O_2$ and therefore improves the oxidation efficiency. The effect of the TSWO method is notable, since the humins conversion ratio increases to 94% with the same $H_2O_2$ content (30% of the initial COD) (e in Fig. 3A).

**Table 2.** Aqueous Products Obtained from Humins Conversion, Identified by GCMS and HPLC Analysis

| NO. | Name | Molecular formula | Similarity (%) | Alkaline-catalytic hydrothermal reaction | TSWO |
|---|---|---|---|---|---|
| 1 | Formic acid | $CH_2O_2$ | - | detected | detected |
| 2 | Acetic acid | $C_2H_4O_2$ | - | detected | detected |
| 3 | 2-Ethylacrolein | $C_5H_8O$ | 85 | detected | not detected |
| 4 | γ-Valerolactone | $C_5H_8O_2$ | 95 | detected | not detected |
| 5 | 6-Methyl-3,6-dihydro-2H-pyran | $C_6H_{10}O$ | 81 | detected | not detected |
| 6 | 2-Methyl-2-cyclopentenone | $C_6H_8O$ | 89 | detected | not detected |
| 7 | Phenol | $C_6H_6O$ | 97 | not detected | detected |
| 8 | *o*-Formylphenol | $C_7H_6O_2$ | 80 | not detected | detected |
| 9 | Dimethylmaleic acid anhydride | $C_6H_6O_3$ | 95 | not detected | detected |
| 10 | *m*-Cresol | $C_7H_8O$ | 85 | detected | detected |
| 11 | 3,4-Dimethyl-2-cyclopenten-1-one | $C_7H_{10}O$ | 89 | detected | not detected |
| 12 | 2,3-Dimethyl-2-cyclopenten-1-one | $C_7H_{10}O$ | 84 | detected | not detected |
| 13 | 5-Hydroxy-2,3-dimethyl-2-cyclopenten-1-one | $C_7H_{10}O_2$ | 81 | detected | not detected |
| 14 | 3-Vinylcyclohexanone | $C_8H_{12}O$ | 83 | detected | not detected |
| 15 | 2-Acetylcyclohexanone | $C_8H_{12}O_2$ | 82 | not detected | detected |
| 16 | *m*-Acetylphenol | $C_8H_8O_2$ | 81 | not detected | detected |

[1] The formic acid and acetic acid were confirmed by HPLC analysis with standard samples, while the others were identified by GCMS analysis with the NIST 08 database.

The oxidant concentration was an important factor during the reaction, and it was obvious that the conversion ratio increased with increasing $H_2O_2$ content (Fig. 3B). Once the addition of $H_2O_2$ reached 75% of the initial COD, a quite high conversion ratio of 99% was obtained. In this reaction condition, the color of the aqueous solution became dark brown in the alkaline state (Fig. 1D), and the color changed to tawny but transparent after the acidification (Fig. 1E). When Fig. 1E is compared with Fig. 1C, it can be concluded that the TSWO was an effective method for degradation of humins.

The reaction routes of TSWO included two main steps, an alkaline-catalytic hydrothermal treatment (step 1) and a wet oxidation (step 2). Interestingly, most of the humins alkaline-catalytic hydrothermal-derived aqueous products (*e.g.*, compounds 3 to 6 and 11 to 14 in Table 2) other than acetic acid and formic acid were not found after step 2. Controlled experiments showed that these aqueous products were further degraded, primarily to acetic acid and other gas products. It should be noted that carboxyl groups could be initially formed on the humins before they were completely degraded. As shown in Fig. 2, a stronger broad FT-IR peak at approximately 2590 $cm^{-1}$ was found on the TSWO derived solid residue, formed by the association effects of carboxyl groups. Importantly, new phenolic products and dimethylmaleic anhydride (*i.e.*, compounds 7, 8, and 16 in Table 2), which were not detected after step 1, were found after step 2. Further experiments confirmed that these phenolic products were formed from the oxidation of the acid-insoluble solid residue formed in step 1. These results indicate two points: (1) The humins have phenolic structures, and these structures are connected by obstinate bonds, which are stable in the direct alkaline-catalytic hydrothermal treatment; and (2) the TSWO technology could effectively degrade these obstinate bonds, forming phenolics and dimethylmaleic anhydride moieties. Moreover, these phenolics and dimethylmaleic anhydride compounds could be finally converted to acetic acid by further oxidation, although the yields seemed low (Table 3). In summary, humins can be completely dissolved in alkaline solution by step 1 and completely degraded to low-molecular weight compounds by step 2.

**Table 3.** Wet Oxidation of Various Feedstocks in Alkaline Solution (0.5 M NaOH) at 150 °C for 1 h Holding Time

| Feedstocks | Acetic acid yield on carbon basis |
|---|---|
| Acid soluble products from humins after alkaline-catalytic hydrothermal treatment[1] | 31.0% |
| Acid insoluble products (or residue) from humins alkaline-catalytic hydrothermal treatment[1] | 25.2% |
| Phenol[2] | 9.2% |
| *m*-Cresol[2] | 1.0% |
| Dimethylmaleic anhydride[2] | 1.5% |

[1] The $H_2O_2$ addition was equivalent to approximately 75% of the initial COD.

[2] The $H_2O_2$ content was approximately 80% of the initial mass of the feedstocks.

## Acetic Acid from Humins

Figure 4A shows the carbon distribution based on the TSWO technology. The overall trend observed is that the yield of aqueous products and solid residue decreased with increasing $H_2O_2$ dosage, forming an increased gas yield with $CO_2$ as the main product. When the $H_2O_2$ addition was equivalent to 85% of the initial COD, 52% and 48% of carbon was distributed into aqueous and gaseous products, respectively, while the carbon in the solid residue was almost negligible.

Acetic acid was the main aqueous product in the TSWO step, with the highest yield reaching 25.6% based on the initial carbon (Fig. 4B) or 37.2% based on the mass of humins with an $H_2O_2$ addition equivalent to 75% of the initial COD. Controlled experiments showed that the aqueous products produced by step 1 formed an acetic acid yield of 31% on a carbon basis (Table 3). These aqueous products formed 7.4% of acetic acid based on the initial carbon of humins, which accounted for approximately 29% of the total acetic acid from the TSWO technology. In other words, approximately 71% of the total acetic acid was formed by alkaline wet oxidation of the acid-insoluble residues formed in step 1. In addition to the high yield of acetic acid, a high purity of acetic acid is desired for the utilization of humins. The purity here is defined as the percentage of organic carbon of acetic acid in the liquid sample *versus* the TOC of the aqueous sample. An acetic acid purity of 46.2% was obtained under the above reaction conditions, and it seems that high $H_2O_2$ content was beneficial to the purity of acetic acid produced (Fig. 4B).

The yields of acetic acid from common biomass (*e.g.*, rice hulls, cellulose, and starch) and other solid materials are between 12% and 22% on a carbon basis, while the yield from humins reaches 25.6% (Table 1), indicating that humins is a good material for acetic acid production. It should be noted that the consumption of alkali, acid and $H_2O_2$, and $CO_2$ production seem obstacles to meet economic requirements, and this TSWO method might be improved. One possible way to avoid $H_2O_2$ consumption is to replace the $H_2O_2$ oxidation step by wet air oxidation (Debellefontaine and Foussard 2000), and further work on this area is being considered.

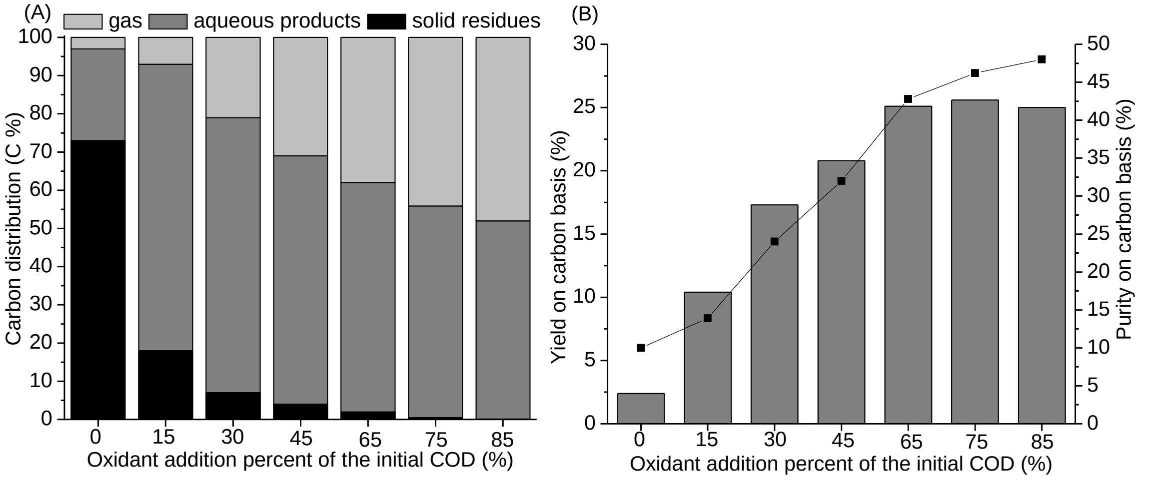

**Fig. 4.** A: Carbon distribution of solid residue, gas, and aqueous products; B: yield and purity of acetic acid

## CONCLUSIONS

1. A new utilization technology for acetic acid production from residual humins was developed through a TSWO method.
2. The humins were completely degraded into gaseous and aqueous products, with acetic acid as the main product.

3. A high acetic acid yield of 25.6% and a purity of 46.2% on a carbon basis were obtained from humins using an $H_2O_2$ addition equivalent to 75% of the initial COD.

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