# EFFECT OF CATALYSTS ON 5-LUMP DISTRIBUTION OF CORNSTALK LIQUEFACTION IN SUB-CRITICAL ETHANOL

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Liquefaction of cornstalk in sub-critical solution of ethanol without and with catalysts ($K_2CO_3$, $Na_2CO_3$ and $ZnCl_2$) was performed in a stainless steel reactor (1 L) at temperatures of 200 to 300 $^oC$. The cornstalk and the products of decomposition were divided into five lumps (gas, organic dissolved, heavy oil, volatile organic compounds, and residue). The effects of reaction temperature and the catalyst amount on the five lump yields were studied. The bio-oils produced with and without catalysts were characterized by GC/MS. Results showed that an increment in the temperature and the addition of catalysts had a synergetic effect on the lumps yield as compared to the non-catalytic experiments, and different catalytic procedures had an important effect on the lump yields and compounds of the bio-oils. The addition of the catalyst enhanced the gas yield and the total conversion rate. A high temperature, lower amount of $Na_2CO_3$, moderate amount of $K_2CO_3$, and a high amount of $ZnCl_2$ were propitious to enhance the heavy oil. The formation of volatile organic compounds with the presence of $ZnCl_2$ and $K_2CO_3$ was less than that in non-catalytic experiments at the higher temperatures. However, a higher conversion temperature had a negative impact on the bio-oils yield from liquefaction of cornstalk with and without catalysts.

*Keywords: Liquefaction; Cornstalk; Catalyst; Lump*

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## INTRODUCTION

The conversion and effective utilization of biomass, which is an abundant and reproducible resource, has increasingly received interest with the rapid development of worldwide industry and the consumption of petroleum and petro-chemicals. Many technologies have been studied in recent years for their possible use in the processing of biomass, such as combustion, pyrolysis, gasification, and liquefaction (Gil et al. 2010). Solid and gas biofuels have a low energy density, which limits their commercial applications. One way to solve this problem is the conversion of the feedstock into liquids fuels. Such liquids have a higher energy density and are easy to store and transport (Veldenl et al. 2010). The one most important method to convert biomass into liquid fuel is the thermochemical conversion in solvents (such as water, ethanol, and acetone) by heat, in which biomass could be decomposed into liquid at mild temperature and atmospheric pressure. A liquid product called bio-oil is a complex mixture of water and organic chemicals, including acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives, and phenolic compounds (Liu et al. 2010).

The bio-oils cannot be used as transportation fuels directly without treatment due to their high oxygen (40 to 50 wt%) and water content (15 to 30 wt%), and low H/C ratios (Pütün 2010). Catalytic pyrolysis liquefaction is a promising way to improve bio-oil quality by removing oxygen, while also increasing the calorific value and stability (Samolada et al. 2000). Alkali metal salts, especially those containing potassium, are excellent promoters of gasification reactions. Fast-growing biomass, which contains large quantities of potassium, may prove to be an excellent source of inexpensive gasification catalyst (Brown et al. 2000). Over the years, many studies on the liquefaction of biomass using catalytic and solvent have been carried out (Akhtar et al. 2010; Hossein et al. 2010). It was found that the alkalis and alkali metal salts were more suitable for obtaining high yields of liquid products from biomass, and solid conversion increased at higher reaction temperature, but the liquid yield did not increase at higher temperature. However, the mechanism of liquefaction using catalyst and solvent has been difficult to study at a molecular level because of the complex liquefaction products. Thermogravimetric analysis (TGA) is a general approach to study the process. It has been employed to investigate the influence of the heating rate on the pyrolysis outcomes as well as the kinetics of the pyrolysis process (Sadhukhan et al. 2008; Li et al. 2008; Park et al. 2009; Velden et al. 2010). However, the TGA is not suitable for studying the effect of solvent on the liquefaction process.

The method of lump analysis has been used to study the complexity of reactive processes (fluid catalytic cracking, catalytic pyrolysis processes, etc.) by lumping the large number of chemical compounds into groups of pseudo-components, according to their boiling points and their molecular characteristics (Meng et al. 2006, 2007; Minkina et al. 2010). Just like the fluid catalytic cracking (FCC) and catalytic pyrolysis processes, the liquefaction of biomass is a complicated process. Therefore, a five-lump model of liquefaction of cornstalk in sub-and super-critical ethanol was established based on the characteristics of the material and products (Liu et al. 2010). The results showed that this is a good way to study the mechanism of catalytic liquefaction by lumping large numbers of chemical compounds together.

In this study, cornstalk was liquefied with and without catalysts ($K_2CO_3$, $Na_2CO_3$, and $ZnCl_2$) in sub-critical ethanol using a stainless-steel autoclave (1 L). The lumps of the liquefaction system were defined based on the characteristics of cornstalk and liquefaction products. The behavior of catalytic liquefaction of cornstalk in ethanol was investigated by studying the effect of catalysts at different temperatures on the lump yields.

## EXPERIMENTAL

### Cornstalk and Solvents

The cornstalk sample investigated in this study was collected from the field of South China Agriculture University, Guangzhou, China. The cornstalk, after undergoing size-reduction by a chipper, was pulverized to pass through a 40-mesh sieve. The flour was extracted with distilled water and ethanol to remove organic dissolved and polar organics, then dried at 105 °C for 24 h and kept in a desiccator at room temperature before being used. The solvents used were distilled water and analytical reagent grade ethanol and acetone.

## Adsorption of Catalysts to Cornstalk

The catalysts ($K_2CO_3$, $Na_2CO_3$, and $ZnCl_2$) used were analytical reagent grade chemicals. The 150 g cornstalk was added into 1000 mL water solution containing catalysts (0.05 mol/L, 0.1 mol/L, 0.2 mol/L). After adsorbing at room temperature for 20 h, the cornstalk was filtered, dried at 105 °C for 24 h and kept in a desiccator at room temperature before used.

## Experimental Procedure

For each run, the cornstalk and ethanol were fed into the magnetically stirred autoclave (volume of 1 L, PARR, USA). The reactor was purged with 2 MPa of nitrogen at room temperature to remove the air/oxygen in the reactor airspace. Then the autoclave was heated to the pre-set final temperature, followed by a holding period of a certain time. The autoclave was then cooled down to room temperature by water. The density of gas was estimated using a gas bag by measuring the bulk and quality of the gaseous component. The bulk of gas was estimated by the way of expelling water from the measuring cylinder. When the autoclave was opened, the reaction mixture was removed for separation. The procedure for the separation is shown in Fig. 1.

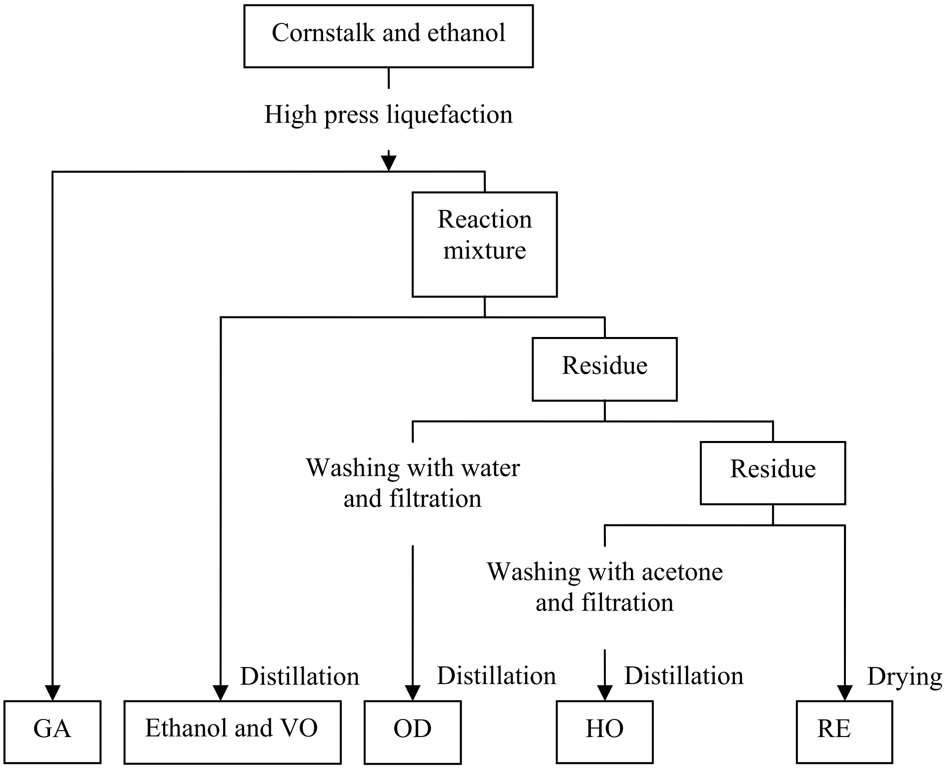

**Fig. 1.** Procedure for separation of products

In order to study the effect of catalysts on the liquefaction of cornstalk in ethanol, the reaction system was divided into gas lump (GA), organic dissolved lump (OD), heavy oil lump (HO), volatile organic compounds lump (VO), and residue lump (RE) based on the characteristics of material and liquefaction products. The entire yield of each lump was calculated on a dry basis and assumed to be ash free. The results obtained in this study were reported using the parameters defined as,

$$Y_{GA} = \frac{V_{GA} \times \rho_{GA}}{W_{Dry} \times (1 - Y_A)} \times 100\% \tag{1}$$

$$Y_{OD} = \frac{W_{OD}}{W_{Dry} \times (1 - Y_A)} \times 100\% \tag{2}$$

$$Y_{HO} = \frac{W_{HO}}{W_{Dry} \times (1 - Y_A)} \times 100\% \tag{3}$$

$$Y_{RE} = \frac{W_{RE} - W_{RE} \times Y_A}{W_{Dry} \times (1 - Y_A)} \times 100\% \tag{4}$$

$$Y_{VO} = 100\% - Y_{GA} - Y_{OD} - Y_{HO} - Y_{RE} \tag{5}$$

where $Y_{GA}$ is the gas yield (wt %), $Y_{OD}$ is the organic solution yield (wt %), $Y_{HO}$ is the heavy oil yield (wt %), $Y_{VO}$ is the volatile organic compounds yield (wt %), $Y_{RE}$ is the residue yield (wt %), $Y_A$ is the ash yield (wt %), $W_{Dry}$ is the mass of cornstalk flour (g), $W_{OD}$ is the mass of dissolved organics (g), $W_{HO}$ is the mass of heavy oil (g), $W_{RE}$ is the mass of residue (g), $V_{GA}$ is the volume of gas (mL), and $\rho_{GA}$ is the density of gas (g/mL).

To ensure reliability of the experimental data, each experiment was repeated twice, and the differences between the results of two tests were below 7.5% of the values.

## Experimental Analyses

Chemical compositions of the bio-oils $(\mathrm{OD} + \mathrm{HO})$ were identified by GC/MS (HP5971) using a 30 mm × 0.25 mm capillary column (DP-5). The gas chromatograph was programmed at 40 $^{o}$C for 2 min, and then followed by a heating rate of 10 $^{o}$C/min to 300 $^{o}$C and holding for 2 min at the final temperature. The injected volume was 0.125 μL. The mass range scanned was from 35 to 500 amu in electron-impact (70 eV) mode. The compounds were identified by comparison with library spectra supplied from the NIST database. The total area of all the peaks was set as 100%, and a relative amount of each peak corresponding to each compound could be calculated according to the ratio of its area to the total area.

A Varian of America Spectr AA 220FS/220Z Atomic Absorption Spectrophotometer equipped with Zeeman background corrector and data processor was used for elemental analysis of the catalysis concentration. All parameters were set and followed strictly according to the manufacturer's instructions using the flame atomization technique.

The ash content of the cornstalk was determined by burning at 650 $^{o}$C. The heating value was obtained from calculation by Dulong's formula. The characteristics of the cornstalks without and with catalysts are shown in Table 1.

**Table 1.** Main Characteristics of the Cornstalk With and Without Catalysts

| Cornstalk | Non- catalyst | $K_2CO_3$ (mol/L) | | | $Na_2CO_3$ (mol/L) | | | $ZnCl_2$ (mol/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1 | 2 | 0.5 | 1 | 2 | 0.5 | 1 | 2 |
| AAS analysis (mg/g) | | | | | | | | | | |
| K | 0.0033 | 0.24 | 0.45 | 0.8 | | | | | | |
| Na | 0.031 | | | | 0.23 | 0.35 | 0.73 | | | |
| Zn | 0.002 | | | | | | | 0.19 | 0.37 | 0.75 |
| Proximate and Ultimate analysis (wt %) | | | | | | | | | | |
| Cellulose | 39.2 | | | | | | | | | |
| Hemicelluloses | 35.1 | | | | | | | | | |
| Lignin | 20.2 | | | | | | | | | |
| Ash | 5.5 | | | | | | | | | |
| Carbon | 49.6 | | | | | | | | | |
| Hydrogen | 5.9 | | | | | | | | | |
| Oxygen | 43.5 | | | | | | | | | |
| Nitrogen | 1.0 | | | | | | | | | |
| HHV (MJ/kg) | 17.4 | | | | | | | | | |

## RESULTS AND DISCUSSION

### Influence of Catalysts on Lump Yields at Various Reaction Temperatures

Catalysts are the crucial parameter to accelerate reaction rates. Selective catalysts can be used for producing certain products, even though many natural and synthetic catalysts can be used (Ates et al. 2009). The effect of catalysts on lump yields at various reaction temperatures are shown in Figs. 2 to 5. The data presented in the figures were obtained from the experimental runs with and without catalysts at various temperatures ranging from 200 to 300 $^{o}$C, at the same time (0 min) and with the same catalyst (if added) concentration. The temperature plays an important role to influence the yield of lumps (GA, OD, HO, VO, and RE) in the process of cornstalk liquefaction with and without the presence of catalysts, as shown in the figures.

*Effect of catalysts on the residue yield*

The effect of catalysts on the RE yield at different temperatures is shown in Fig. 2. As shown, in the whole range of the temperatures tested, the RE yield from liquefaction of cornstalk with and without catalysts decreased continuously with increasing reaction temperature. Comparing these runs of cornstalk liquefaction without catalyst and with catalysts ($K_2CO_3$, $Na_2CO_3$, and $ZnCl_2$), the RE yield strongly decreased when the three catalysts were added. Moreover, the RE yield under the condition of the addition $K_2CO_3$ and $Na_2CO_3$ were found to be almost the same. Thus, it might be generally concluded that the addition of the catalysts significantly enhanced the conversion rates (100% - $Y_{RE}$).

*Effect of catalysts on the gas yield*

Figure 3 shows the effect of catalysts on the GA yield at different temperatures. As shown, the yield of GA strongly depended on the reaction temperature in the range of 200 to 300 $^{o}$C.

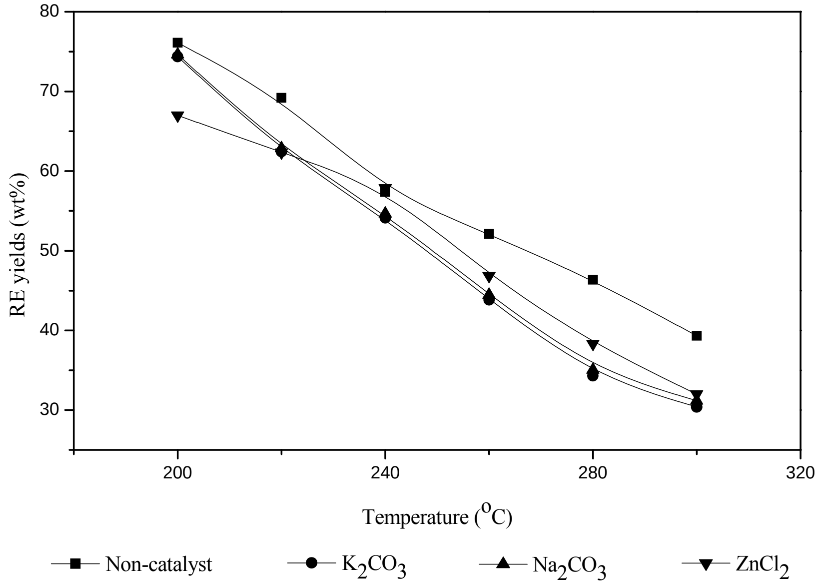

**Fig. 2.** Effect of catalyst on the RE yield at various temperatures

Regardless of which catalyst was present, the GA yield showed an identical trend, and GA yield increased with increasing reaction temperature. The addition of the three catalysts significantly enhanced the lump of GA over the whole temperature range (200 to 300 °C). It was worth noting that beyond 240 °C the effect of $ZnCl_2$ on the GA yield was more strongly increased as compared to other catalysts used in the procedure. Therefore, in the presence of zinc chloride, an increase in the GA yield was observed as compared to those obtained by pure ethanol and other catalysts ($K_2CO_3$ and $Na_2CO_3$) runs at the higher temperatures.

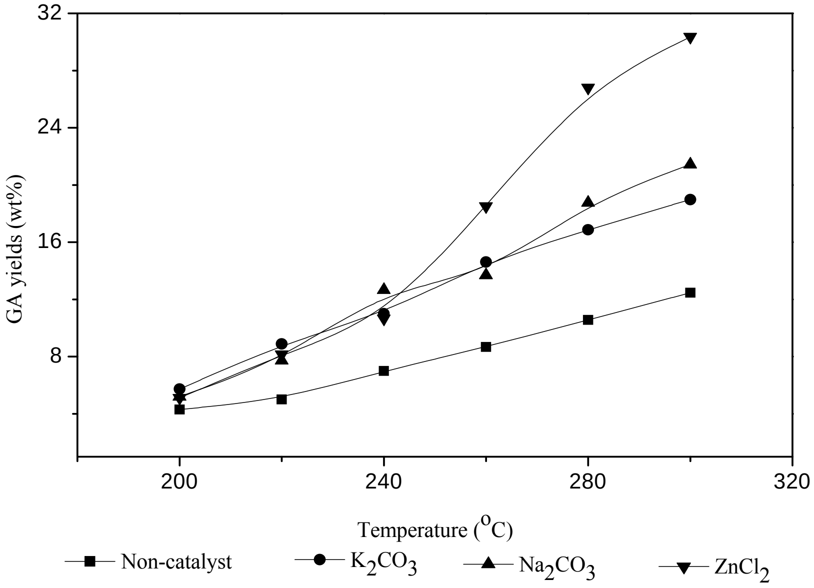

**Fig. 3.** Effect of catalyst on the GA yield at various temperatures

*Effect of catalysts on the volatile organic compounds yield*

Figure 4 shows the effect of catalysts on the VO yield at different temperatures. Obviously, the temperature is an important factor affecting the VO yield. That is, the VO yields in all of the liquefaction of cornstalk runs increased with increasing temperature. The addition of $K_2CO_3$ increased the VO yield as compared to the results obtained in non-catalyst runs over the whole range of the temperatures tested. Different results of VO yield were shown for other catalysts ($ZnCl_2$ and $Na_2CO_3$). In the presence of $ZnCl_2$ and $Na_2CO_3$, the formation of VO was less than pure ethanol runs when the temperature reached 240 $^oC$ and 300 $^oC$, respectively. The possible reason may be that products of the degradation of VO were transformed into GA (see Fig. 3).

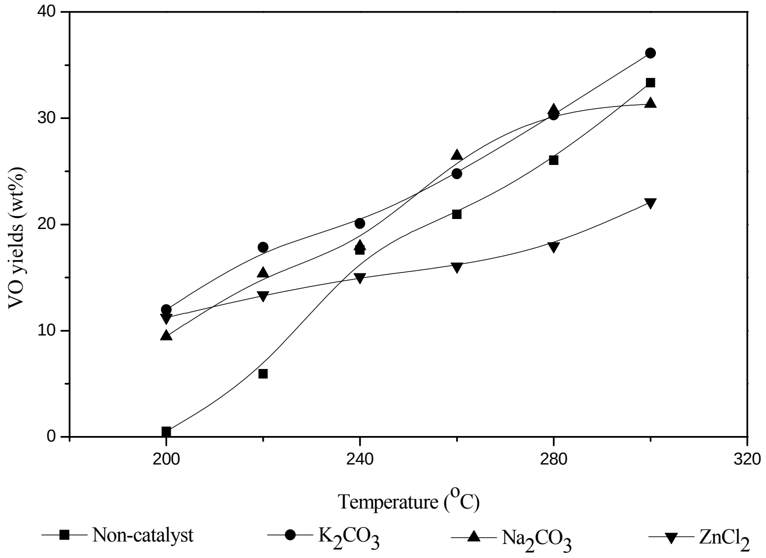

**Fig. 4.** Effect of catalyst on the VO yield at various temperatures

*Effect of catalysts on the bio-oil (organic dissolved and heavy oil) yield*

Figure 5 shows the effect of catalysts on the bio-oil at different temperatures. Clearly, the yield of OD was lower when using $Na_2CO_3$ than the non-catalyst run. $K_2CO_3$ and $ZnCl_2$ appeared to be more effective than $Na_2CO_3$ for promotion of OD formation at the lower tested temperature range. However, a disadvantage of $K_2CO_3$ and $ZnCl_2$ may be that they cannot effectively promote the OD production at the higher temperature as compared to the non-catalyst run. For the three catalysts, the catalytic effects on the HO formation became more significant at the higher temperatures. For instance, the HO yield increased from 9.3% (non-catalyst) to 12.5% (with $K_2CO_3$) at 280 $^oC$, from 8.8% (non-catalyst) to 10.4% (with $Na_2CO_3$) at 300 $^oC$, and from 9.4% (non-catalyst) to 11.2% (with $ZnCl_2$) at 260 $^oC$, respectively. One advantage of this approach is that the three catalysts increased the bio-oil $(OD+HO)$ yield as compared to pure ethanol at higher temperatures. The bio-oils yield from liquefaction of cornstalk with $K_2CO_3$, $ZnCl_2$, and $Na_2CO_3$ were higher than non-catalyst runs after the reaction reached 240, 260, and 300 $^oC$, respectively. Comparatively, the liquefaction of cornstalk for $K_2CO_3$ showed a higher value than those of $ZnCl_2$ and $Na_2CO_3$ for the bio-oil yield and OD yield. The reduction in the bio-oil yield in the presence of $ZnCl_2$ and $K_2CO_3$ catalysts at a higher temperature were due to cracking of the liquid product to GA and VO by isomerization, dehydration, and fragmentation. It can be concluded that $ZnCl_2$ and $K_2CO_3$ catalysts, used with cornstalk in ethanol, maximized the bio-oil yield, depending on the temperature. At moderate temperatures, the addition of catalysts increased the bio-oil yield as compared to that of the non-catalytic experiments.

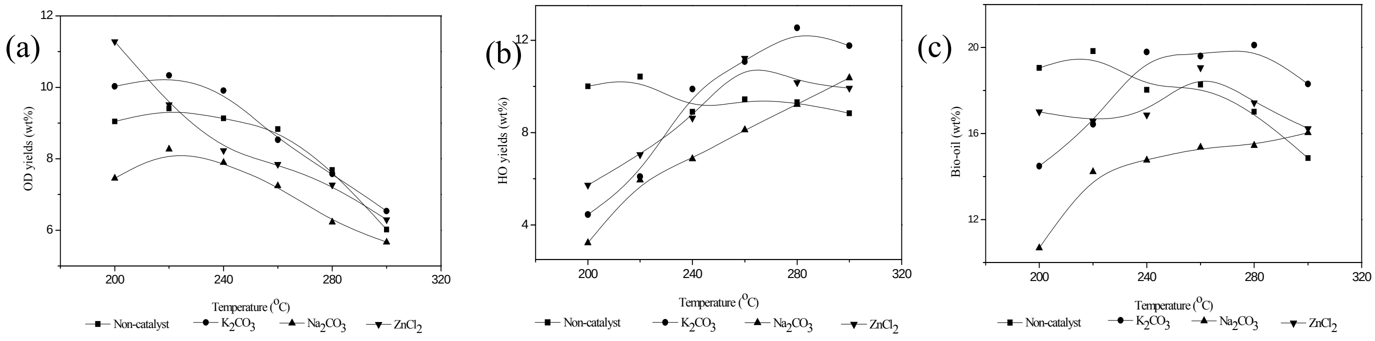

**Fig. 5.** Effect of catalyst on the liquid products at various temperatures. (a) Effect of catalyst on the OD yield. (b) Effect of catalyst on the HO yield. (c) Effect of catalyst on the bio-oil yield.

## Effect of Catalyst Amount on Lump Yields

The effect of catalyst on the lump yields at different temperatures was studied. To investigate the effect of catalyst amount on the lumps yield, experimental measurements were carried out under the condition of 260 °C, 5 g cornstalk, 50 mL ethanol, and different catalyst amounts (0.05 mol/L, 0.1 mol/L, and 0.2 mol/L). The results in terms of the lump yields at different amounts of catalysts are shown in Figs. 6, 7, and 8.

### *Effect of $K_2CO_3$ amount on the lump yields*

Figure 6 shows the effect of $K_2CO_3$ amount on the lump yields from liquefaction of cornstalk. The results showed that the amount of $K_2CO_3$ had a strong influence on the lump distribution from Fig. 6. The yield of RE decreased with the increasing amount of $K_2CO_3$. These results showed that a further addition of $K_2CO_3$ enhanced the conversion rates of cornstalk liquefaction. However, the addition of $K_2CO_3$ favored to degradation of OD yield at low catalyst concentrations. When the amount of catalyst further increased, the OD yield was higher than the non-catalyst runs at 260 °C.

It was obvious that the $K_2CO_3$ amount had a contrary effect on the VO yield: the VO yield increased from 21.0% (non-catalyst) to 24.3% (0.1 mol/L), and then decreased to 22.9% at the higher catalyst amount (0.2 mol/L). The GA further increased with the increase in catalyst amount. These results can be attributed to the increased number of catalytic active sites at a higher catalyst amount. A moderate amount of $K_2CO_3$ could also improve the HO yield as compared with that of the non-catalytic and lower amount catalyst runs. For example, the HO yield of 8.6% and 8.9% were obtained at the catalyst amount of 0.05 mol/L and 0.2 mol/L, respectively, which were lower than the non-catalyst examination (9.4%); the maximal HO yield (11.1%) was obtained at the catalyst amount of 0.1 mol/L.

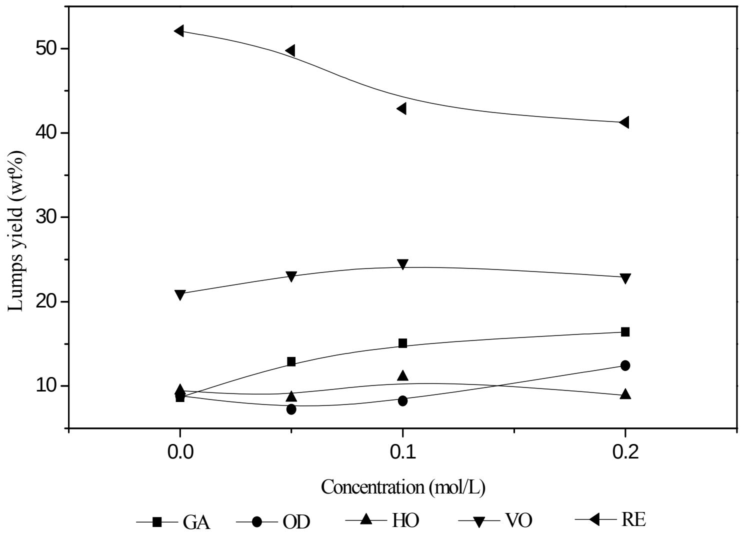

**Fig. 6.** Effect of $K_2CO_3$ concentration on the lump yields

*Effect of $Na_2CO_3$ amount on the lumps yield*

Figure 7 shows the effect of $Na_2CO_3$ amount on the lump yields from liquefaction of cornstalk. Although the RE yield decreased from 52.1% (non-catalyst) to 45.4% (0.05 mol/L) under the addition of $Na_2CO_3$, the RE yield decreased slightly with the further increase in catalyst amount. This result showed that the amount of $Na_2CO_3$ had little influence on the conversion rates of cornstalk liquefaction. The yield of GA obtained from liquefaction of cornstalk increased from 8.7% (non-catalyst) to 14.6% (0.2 mol/L) with increasing amounts of $Na_2CO_3$ (Fig. 7). The catalyst concentration had a great influence on the HO and OD yields, and an increment in the catalyst concentration could inhibit the production of HO and enhance the OD yield, respectively. At a low and moderate amount of the catalyst, the VO yield increased as compared to that of the non-catalytic experiment and a higher amount of catalytic experiment. The VO yields of 26.37% and 26.45% were obtained with the catalyst amounts of 0.05 mol/L and 0.1 mol/L, respectively, which were higher as compared to the yields of 21.0% (non-catalyst) and 22.3% (0.2 mol/L).

Figure 8 shows the effect of $ZnCl_2$ concentration on the lump yield from liquefaction of cornstalk. As shown in the figure, the RE yield decreased slightly from 48.5% (0.05 mol/L) to 46.7% (0.2 mol/L) with increasing the amount of $ZnCl_2$. Therefore, further addition of $ZnCl_2$ could not markedly increase the total conversion rates. In the previous section it was shown that the HO yield decreased with increasing $Na_2CO_3$ catalyst amount. Comparatively, in the presence $ZnCl_2$ and $Na_2CO_3$, the results were very diverse. As seen from Fig. 8, the HO and OD yields increased with increasing amounts of catalyst. However, the concentration of $ZnCl_2$ had an important influence on the yields of GA and VO, and it is worth noting that the yields of GA and VO were negatively correlated with the increases in amount of catalyst. The GA yield increased about 11.0% from 12.7% (0.05 mol/L) to 23.7% (0.2 mol/L), and the VO yield decreased about 13.1% from 22.5% (0.05 mol/L) to 9.4% (0.2 mol/L) from Fig. 8.

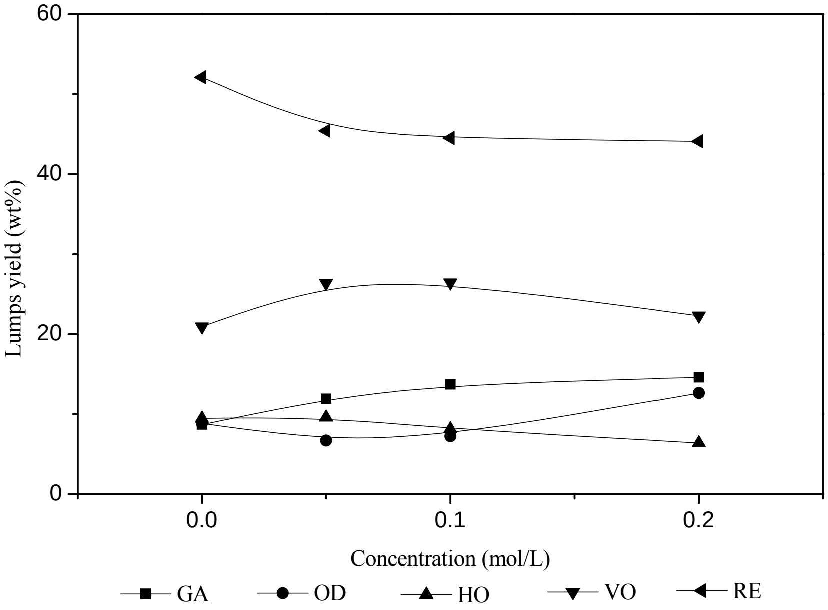

**Fig. 7.** Effect of $Na_2CO_3$ concentration on the lump yields

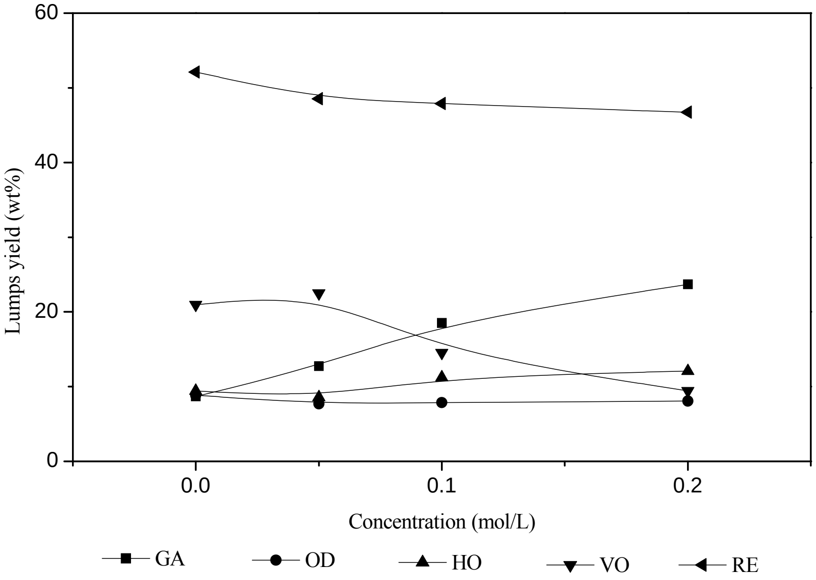

**Fig. 8.** Effect of $ZnCl_2$ concentration on the lump yields

### *Effect of $ZnCl_2$ amount on the lumps yield*

In our previous study (Liu et al. 2010), we found that there was a reversible reaction between the HO and VO from liquefaction of cornstalk in sub-and super-critical ethanol without catalyst. However, the addition of catalysts accelerated the reaction rate and changed the lump reaction pathways. This study showed that there was competitive reaction between GA and VO in the presence of $ZnCl_2$, which was similar to that observed in the study of GA yield at different temperatures in the presence of $ZnCl_2$.

### *GC/MS analysis of bio-oils*

Gas chromatography/mass spectrometry (GC/MS) has become a quick, convenient and powerful tool for characterizing complex and heterogeneous bio-oil samples (Sobeih et al. 2008). Bio-oil contains a large number of different compounds, making it very difficult to identify each of the compounds. Therefore, in this paper, focus is given to key compounds. Table 2 shows the major components of the bio-oils obtained from liquefaction of cornstalk at standard condition (reaction temperature of 300 $^oC$, catalyst amount of 0.1 mol/L (if added), 5 g cornstalk and 50 mL ethanol) using GC/MS. As a result of the disintegration of the cornstalk with and without the presence of catalysts, the liquefaction of cornstalk was transformed into products having different molecular structures. This showed that the use of catalysts had an important effect on the formation of various compounds in the bio-oils.

During the studies conducted in recent years, the bio-oil products obtained with biomass liquefaction have been analyzed in detail using GC/MS. Huang et al. (2011) studied the thermo-chemical liquefaction characteristics of microalgae in sub- and supercritical ethanol and found that fatty acid ethyl ester compounds were the major compounds identified in the bio-oil, followed by fatty acid methyl/dimethyl ester, organic acids, heterocyclic nitrogen compounds, and long-chain alkanes. Aguado et al. (2000) studied the flash pyrolysis of sawdust at 350 to 700 $^oC$ and showed that formaldehyde, methanol, acetic acid, furfural, and several phenols were the main compounds presents in the bio-oil. As shown in Table 2, the most important compounds present in cornstalk bio-oils are furfural, phenols, acids, and esters.

**Table 2.** GC/MS Analysis Results for the Bio-Oils Obtained from the Liquefaction of Cornstalk With and Without Catalysts at 300 $^oC$.

| No. | RT (min) | Compound | Content (%) | | | | Formula | Mw |
|---|---|---|---|---|---|---|---|---|
| | | | Non-catalyst | $Na_2CO_3$ | $ZnCl_2$ | $K_2CO_3$ | | |
| 1 | 5.57 | Propanoic acid, 2-hydroxy-, ethylester, (S)- | | | 4.0 | | $C_5H_{10}O_3$ | 118 |
| 2 | 6.04 | Furfural | 16.0 | 3.0 | 25.4 | 15.4 | $C_5H_4O_2$ | 96 |
| 3 | 6.62 | 2-Furanmethanol | | 3.4 | | | $C_4H_4O_2$ | 84 |
| 4 | 7.94 | Butane, 1,1-diethoxy- | | | 5.1 | | $C_8H_{18}O_2$ | 146 |
| 5 | 9.45 | Butane, 1,1-diethoxy-3-methyl- | 5.3 | | 1.1 | 1.4 | $C_9H_{20}O_2$ | 160 |
| 6 | 10.25 | Phenol | 1.0 | 8.1 | 1.4 | 8.3 | $C_6H_6O$ | 94 |
| 7 | 13.19 | 2-Furaldehyde diethyl acetal | 6.5 | | 1.5 | | $C_9H_{14}O_3$ | 170 |
| 8 | 13.54 | Phenol, 2-methoxy- | 1.9 | 5.6 | | 4.6 | $C_7H_8O_2$ | 124 |
| 9 | 15.46 | Phenol, 4-ethyl- | 2.9 | 4.1 | | 5.3 | $C_8H_{10}O$ | 122 |
| 10 | 15.57 | Benzoic acid, ethyl ester | | 4.5 | 2.4 | 6.9 | $C_9H_{10}O_2$ | 150 |
| 11 | 15.83 | Pterin-6-carboxylic acid | | | | 3.1 | $C_7H_5N_5O_3$ | 207 |
| 12 | 16.28 | Benzofuran, 2,3-dihydro- | | 4.3 | | 8.3 | $C_8H_8O$ | 120 |
| 13 | 17.24 | Ethyl oxamate | | | | 3.2 | $C_4H_{10}O_3N$ | 117 |
| 14 | 20.36 | 1,3-Propanediamine, N-methyl- | | | | 3.7 | $C_4H_{12}N_2$ | 88 |
| 15 | 21.77 | Hexadecanoic acid, ethyl ester | 2.0 | 4.9 | 3.5 | | $C_{18}H_{36}O_2$ | 284 |

## CONCLUSIONS

1. Lump analysis was found to be effective for the study of biomass liquefaction. An increase in the temperature and the use of catalysts had a synergetic effect on the lump yields as compared to the non-catalytic experiments, and different catalytic procedures had different effects on liquefaction of cornstalk.
2. The addition of the three catalysts significantly enhanced the lump of GA and the total biomass conversion at the temperatures tested, and liquefaction at high temperatures could increase the HO yield as compared to that of the non-catalytic runs. The formation of VO was less than non-catalytic experiments after the temperature reached to 240 and 300 $^{o}$C in the presence of $ZnCl_2$ and $Na_2CO_3$, respectively. The bio-oil yield increased and the OD yield decreased at the moderate and high liquefaction temperatures in the experiments without and with catalysts.
3. Further increasing the amount of the three catalysts increased the GA, OD, and RE yields, but the more $Na_2CO_3$ and $ZnCl_2$ could not markedly decrease the RE yield. A lower amount of $Na_2CO_3$, moderate amount of $K_2CO_3$, and a higher amount $ZnCl_2$ were favored to enhance the HO yield.
4. The use of different types of catalysts had significant effects on the formation of various compounds in the bio-oils.

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