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Mechanism of Esters Formation during Cellulose Liquefaction in Sub- and Supercritical Ethanol

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Cornstalk cellulose was liquefied in sub- and supercritical ethanol using an autoclave at 320 °C with 160 mL of ethanol. The effects of reaction time on esters formation during cellulose liquefaction were investigated. The yield of esters was 10.0% at 30 min, increasing to 19.1% after 60 min. Ethanol favored esters formation from cellulose liquefaction. The liquid products at different reaction time were analyzed by FT-IR and GC/MS. The results showed that many free radicals were produced in sub-/super-critical ethanol interactions. Cellulose was converted to active cellulose, which was transformed into large molecular acids by dehydration, decomposition, ring-opening reactions, isomerization, and aldol condensation, and then formed ethyl esters such as ethyl lactate by esterification. In addition, ethyl esters were decomposed to acids, alcohols, and other compounds with increasing reaction time in the presence of ethanol free radicals. Using these results, a reaction network for the formation of ethyl esters from cellulose in sub- and supercritical ethanol was proposed.

INTRODUCTION

Biomass is in a form of solar energy that is stored as chemical energy. Its clean efficient conversion and utilization has received great attention. Biomass has been mainly converted to energy by thermochemical approaches, including pyrolysis, gasification, and direct combustion (Li *et al*. 2009). Bio-oil has been found to be an excellent liquid fuel and a source of raw materials for the chemical industrial (Luo *et al*. 2004). The quality of bio-oil has a close relationship with the reaction conditions and equipment (Yanik *et al*. 2007).

Supercritical liquefaction is increasingly being considered for biomass conversion to fuels and platform chemicals (Levine *et al*. 2010; Poudel and Oh 2012). The supercritical fluid has many advantages such as the liquid and gas properties (Chumpoo and Prasassarakich 2010; Williams and Onwudili 2006). The major organic components of biomass liquefaction products can be classified as esters, ketones, acid anhydrides, phenolic compounds, furan derivations, and alcohols. One of the major components in these products is esters. These esters, such as levulinic acid ester, are widely used in chemical, food, fuel, resins, and other fields. Researchers have determined that the relative amounts of esters derived from rice straw and corn stalk in sub- and supercritical fluid were as high as 26.9% to 42.7% (Tang *et al*. 2009; Zheng *et al*. 2013), and the levulinic acid ester accounts for 13.8% to 40.7% (Mao *et al*. 2010; Rataboul and Essayem 2011). Previous work by the authors has shown that the content of ethyl esters is about 26.9% in

light oil and 29.6% in heavy oil obtained from cornstalk cellulose liquefaction in sub-and supercritical ethanol (Zheng *et al*. 2012).

Currently, many researchers are focusing on the process optimization of esters production from biomass, and only few are studying the reaction mechanism. Therefore, there is little information on the reaction pathways and transformation selectivity of the cellulose liquefaction process. In this study, cornstalk cellulose liquefaction in sub- and supercritical ethanol was investigated to better understand the reaction mechanism of esters production by characterizing liquid products with Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectroscopy (GC-MS).

EXPERIMENTAL

Materials

Cornstalks were collected from a farm in Guangzhou, China. The feedstock was milled to obtain fine powder by passing through a 40-mesh sieve. The powder was dried at 105 °C for 24 h before use. Anhydrous ethanol, acetone, and sodium hydroxide were of analytical grade. Sodium chlorite was of industrial grade.

Cornstalk cellulose preparation

Water-soluble products in cornstalk cellulose were removed according to GB/T 2677.1-93–GB/T 2677.10-95 (Tao *et al*. 2013). Lignin was treated with a sodium chlorite solution to obtain holocellulose. The insoluble residue (cornstalk cellulose) was prepared by treating holocellulose with sodium hydroxide solution; this residue was then dried at 105 °C for 24 h and kept in a desiccator at room temperature.

Methods

Experimental procedure

The liquefaction experiments were carried out using a 1.0-L high-pressure high-temperature stainless steel reactor (PARR 4521M, USA) rated to a working pressure of 2000 psi and a working temperature of 350 °C. In a typical liquefaction experiment, the reactor was loaded with 160 mL ethanol and 15 g of cellulose. Then, the reactor was purged with nitrogen for 8 min. Agitation was set at 250 rpm, which was maintained for all experiments. The reactor was heated up to setting temperature. Timing began when the temperature reached 320 °C. The reaction was maintained for a set time. After the reaction was completed, the reactor was removed from the electric furnace, cooled down rapidly to 40 °C in cold water, and the gas (GAS) collected with a gas-bag. The autoclave was opened, and the liquefaction products were collected into a beaker by washing the reactor with ethanol. The liquid and solid products in the mixture were separated by rotary evaporation, using acetone as a solvent. The temperature of the rotary evaporation was 60 °C. Soxhlet extraction was used to deal with the solids in the flask. The liquid portion was termed bio-oil, and the solid portion was denoted residue. The results obtained in this study were reported using the following parameters,

$$w_{BO} = \frac{m_{BO}}{m} \times 100\% \tag{1}$$

$$w_{RE} = \frac{m_{RE}}{m} \times 100\% \tag{2}$$

$$x = 1 - \frac{m_{RE}}{m} \times 100\% \tag{3}$$

$$w_{BOI} = w_{RI} \times w_{BO} \times 100\% \tag{4}$$

where w_{BO} is the yield of bio-oil (%), w_{RE} is the yield of the residue (%), w_{BOI} is the yield of bio-oil ingredients (%), w_{RI} is the relative amount of bio-oil ingredients (%), x is the conversion of cornstalk cellulose , m_{BO} is the weight of bio-oil (g), m_{RE} is the weight of the residue (g), and m is the weight of raw material (g).

Chemical Analysis

The bio-oil was analyzed using a gas chromatograph equipped with a mass spectroscope (Finnigan Co., USA) and a Hewlett-Packard (USA) HP-1 column (30 mm x 0.25 mm). Both the injector and detector were kept at 250 °C, and the flow of the carrier gas (He) was 1.0 mL·min^{-1}. The oven program was a 10 min isothermal at 40 °C, followed by a heating rate of 100 °C min^{-1} to 120 °C and hold for 1 min; then a heating rate of 50 °C min^{-1} to 250 °C and hold for 10 min. The injected volume for analysis was 0.5 μL. The mass range scanned was from 35 to 335 amu in electron-impact (70 eV) mode. Data were acquired and processed using Chemstation software (Agilent Technologies Inc., 7890, USA). The compounds were identified by comparing the mass spectra with KIST library data (Tao *et al*. 2013). The bio-oil was also analyzed by a Bruker EQUIVOX55 FT-IR (Bruker Co., Germany) to investigate its functional groups.

RESULTS AND DISCUSSION

Effect of Reaction Time on Yields

The effect of reaction time on the products distribution is shown in Fig. 1. The bio-oil yield increased from 16.07% to 51.42% as the reaction time increased from 0 to 120 min. The residue decreased from 58.31% to 13.86% as the reaction time increased. Higher conversion was obtained in 120 min.
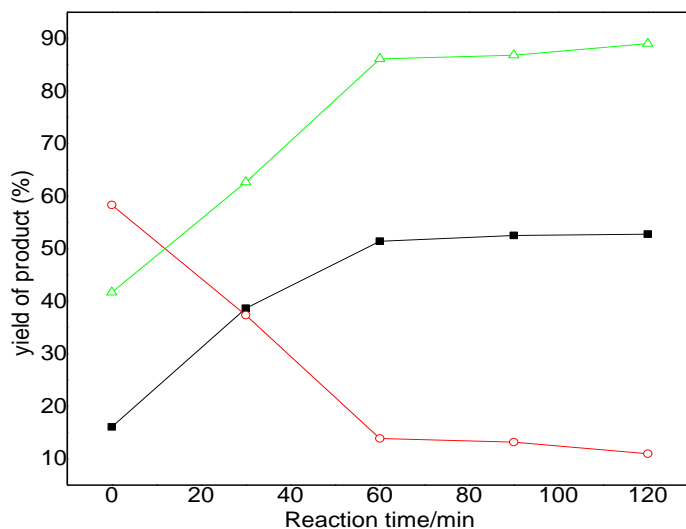

Fig. 1. Effects of reaction time on products distribution and cellulose conversion: ■ yield of liquid product; ○ yield of residue ; △ conversion of cellulose

The results indicated that cellulose was easier to decompose with increasing reaction time. As the reaction progresses, ethanol can dissolve more reactant and products. At the same time, ethanol can provide free radicals such as H·, HO·, CH$_3$·, and CH$_3$CH$_2$·. These free radicals can stabilize liquefaction intermediates and prevent them from forming residue. The free radicals also promote cellulose liquefaction to form low-molecular weight compounds (Li *et al*. 2004).

Effect of Reaction Time on Esters

The yield of esters is shown in Fig. 2. The yield of esters increased from 5.8% to 19.1% as reaction time increased from 30 to 60 min. It may be that the presence of ethanol could promote cellulose liquefaction, dehydration, and esterification to form esters. With further increasing reaction time, the yield of esters decreased. The increased reaction time may have increased the activity of alcohol radicals, which promoted ester decomposition to acids, aldehydes, ketones, and other compounds (Li *et al.* 2009).
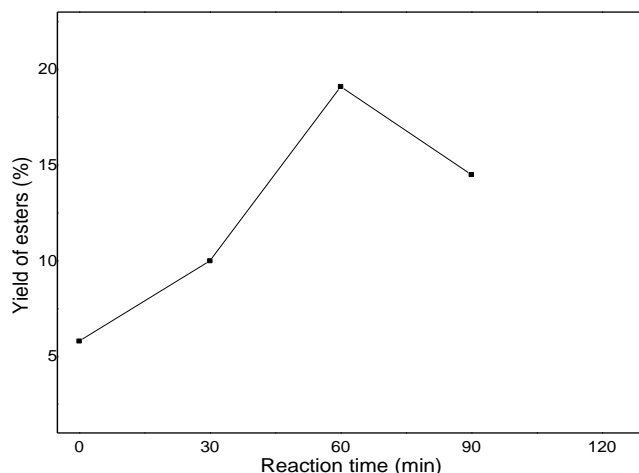

Fig. 2. Effects of reaction time on the yield of esters in 160 mL ethanol at 320 °C

GC-MS Analysis

The bio-oil obtained from cellulose liquefaction at 320 °C at different reaction times was analyzed by GC-MS to investigate the effect of reaction time on esters. The yields of typical compounds identified in bio-oil are presented in Table 1.

Bio-oil also was obtained from cellulose liquefaction at 60 min at different reaction temperature was analyzed by GC-MS. The yields of typical compounds identified in bio-oil are presented in Table 2.

As shown in the tables, the bio-oil was mostly composed of esters, ketones, and acids. The yields and components of bio-oil were different at different reaction conditions. When the reaction time was increased to 60 min at 320 °C, the yield of esters, ketones, and acids obtained from cellulose liquefaction increased. This could be because the presence of more ethanol free radicals accelerates the decomposition, decarboxylation, and isomerization of cellulose to form products (Wang *et al.* 2007). The major esters were ethyl esters. Cellulose can undergo reactions such as cracking, ring-opening, aldol condensation, and dehydration to form aliphatic ketones (Tao *et al.* 2013). Furthermore, esters are created by dehydration, cyclization, and isomerization of cellulose. Longer reaction times would result in the cracking of ethyl esters and their conversion to small molecular compounds such as ketones and alcohols.

Table 1. GC/MS Analysis Results for BIO-OIL Obtained from Cornstalk Cellulose Liquefaction in Sub- and Supercritical Ethanol at Different Reaction Time

RT t/min	Name of compound	Formula	Area (%)				
			0 min	30 min	60 min	90 min	120 min
Esters							
8.21	propanoic acid, 2-hydroxy-, ethyl ester	$C_5H_{10}O_3$	0.83	2.03	3.46	2.67	2.92
9.07	butanoic acid, 2-hydroxy-, ethyl ester	$C_6H_{12}O_3$	0.96	1.11	1.70	1.55	1.91
9.28	acetic acid, hydroxy-, ethyl ester	$C_4H_8O_3$	1.25	2.61	3.00	2.11	1.41
11.48	propanoic acid, 2-methyl-, ethyl ester	$C_6H_{12}O_2$	2.12	-	4.97	4.75	-
12.60	pentanoic acid, 4-oxo-, ethyl ester	$C_7H_{12}O_3$	-	0.68	0.98	0.67	0.58
13.79	butanedioic acid, diethyl ester	$C_8H_{14}O_4$	-	0.47	0.85	0.66	0.62
15.80	pentanedioic acid, diethyl ester	$C_9H_{16}O_4$	0.64	0.49	0.91	0.80	0.82
17.60	4-oxepincarboxylic acid, 2,3,6,7-tetrahydro-, ethyl ester	$C_9H_{14}O_3$		-	0.84	0.88	0.85
Ketones							
8.58	2-pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	5.76	11.99	14.6	16.5	19.5
11.47	2(3h)-furanone, dihydro-3-hydroxy-4,4-dimethyl-, (r)-	$C_6H_{10}O_3$	-	2.90	-	-	5.06
13.09	2,3-dideuterio-4-t-butyl-cyclohexanone		-	0.94	-	-	-
16.07	3,5-dimethyl cyclopentenolone	$C_7H_{10}O_2$		-	0.75	0.60	-
16.77	2-cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	1.87	1.72	1.95	1.05	0.84
17.18	cyclohexanone, 2-acetyl-	$C_8H_{12}O_2$	-	-	-	0.50	0.54
18.04	3-ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	-	0.82	1.18	0.93	0.62
18.65	2-cyclohexen-1-one,2-hydroxy-3-methyl-6(1-methylethyl)	$C_{10}H_{16}O_2$	0.67	-	-	1.00	1.31
21.26	5-dodecanone	$C_{12}H_{24}O$	-	0.78	-	-	-
8.58	2-pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	9.67	11.99	14.6	16.5	19.5
Acids and anhydride							
13.13	diethyl methylsuccinate	$C_9H_{16}O_4$	0.34	-	1.49	0.14	1.16
16.27	ethyl 4-hydroxybutanoate	$C_6H_{12}O_3$	1.57	-	-	-	0.32
22.23	Methy-2-diazo-4(1-methyl-1-cyclohexyl)-3-oxobutanoate	$C_{12}H_{18}N_2O_3$	-	0.66	-	-	-
33.33	hexanoic acid	$C_6H_{12}O_2$	-	-	-	4.38	-
Alcohols				-	-	-	-
12.15	1,2-propanediol	$C_3H_8O_2$	-	-	0.84	0.78	0.91
10.54	4-heptanol	$C_7H_{16}O$	0.97	0.61	1.87	1.81	2.60
13.65	2h-pyran-2-methanol, tetrahydro-	$C_6H_{12}O_2$	0.76	-	-	-	0.42
Furan and derivatives							
10.63	Furan,2-butyltetrahydro-	$C_8H_{16}O$	0.55	-	0.24	-	-
13.69	2H-Pyran-2-methnol, tetrahydro-	$C_6H_{12}O_2$	-	-	0.49	-	0.45
16.48	2H-Pyran-2-one, tetrahydro-	$C_5H_8O_2$	-	-	0.27	0.21	-

Table 2. GC/MS Analysis Results for BIO-OIL Obtained from Cornstalk Cellulose Liquefaction in Sub- and Supercritical Ethanol at Different Reaction Temperature

RT t/min	Name of **compound**	Formula	Area (%)		
			280℃	300℃	320℃
Esters					
8.21	propanoic acid, 2-hydroxy-, ethyl ester	$C_5H_{10}O_3$	1.58	3.11	3.46
9.07	butanoic acid, 2-hydroxy-, ethyl ester	$C_6H_{12}O_3$	0.75	2.32	1.70
9.28	acetic acid, hydroxy-, ethyl ester	$C_4H_8O_3$	1.47	1.81	3.00
10.56	butanoic acid, 2-hydroxy-3-methyl-, ethyl ester	$C_7H_{14}O_3$		2.44	
11.46	3-hydroxy-4,4-dimethyl butanolactone dit pantolactone	$C_6H_{10}O_3$	2.12	-	
11.48	propanoic acid, 2-methyl-, ethyl ester	$C_6H_{12}O_2$		-	4.97
12.60	pentanoic acid, 4-oxo-, ethyl ester	$C_7H_{12}O_3$	0.38	-	0.98
13.79	butanedioic acid, diethyl ester	$C_8H_{14}O_4$	0.29	0.68	0.85
15.80	pentanedioic acid, diethyl ester	$C_9H_{16}O_4$	0.28		0.91
17.60	4-oxepincarboxylic acid, 2,3,6,7-tetrahydro-, ethyl ester	$C_9H_{14}O_3$			0.84
Ketones					
8.58	2-pentanone, 4-hydroxy-4-methyl	$C_6H_{12}O_2$	12.67	16.11	14.64
11.47	2(3h)-furanone, dihydro-3-hydroxy-4,4-dimethyl-, (r)-	$C6H_{10}O_3$	3.47	-	
13.09	2,3-dideuterio-4-t-butyl-cyclohexanone			-	
16.07	3,5-dimethyl cyclopentenolone	$C_7H_{10}O_2$		-	0.75
16.11	1,3-cyclopentanedione,2,4-dimethyl-	$C_7H_{10}O_2$		0.54	
16.77	2-cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	0.72	-	1.95
16.79	1,2-cyclopentanedione, 3-methyl-	$C_6H_8O_2$		1.01	
17.18	cyclohexanone, 2-acetyl- (cas)	$C_8H_{12}O_2$		0.73	
17.65	1,3-cyclopentanedione, 2-ethyl-2-methyl-	$C_8H_{12}O_2$		1.3	
18.04	3-ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	0.38	1.32	1.18
21.26	5-dodecanone	$C_{12}H_{24}O$			
29.32	1,3,5-triazine-2,4(1h,3h)-dione, 6-(methylamino)-	$C_4H_6N_4O_2$	0.64		
Acids and anhydride					
11.49	butanoic acid, anhydride	$C_8H_{14}O_3$		6.26	
13.13	diethyl methylsuccinate	$C_9H_{16}O_4$			1.49
25.78	(d,l)-malic acid	$C_4H_6O_5$	1.14		
33.33	hexanoic acid	$C_6H_{12}O_2$			
Alcohols					
9.84	ethanol, 2,2-diethoxy-	$C_6H_{14}O_3$	0.90		
12.15	1,2-propanediol	$C_3H_8O_2$			0.84
10.54	4-heptanol	$C_7H_{16}O$	0.51		1.87
19.28	1,8-nonanediol, 8-methyl-	$C_{10}H_{22}O_2$	0.73		0.82
Furan and derivatives					
13.51	2-furanmethanol	$C_5H_6O_2$			0.97
13.69	2h-pyran-2-methnol, tetrahydro-	$C_6H_{12}O_2$			

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FT-IR Analysis

The structure of bio-oil products produced at various reaction times was analyzed using FT-IR. The results are shown in Fig. 3.
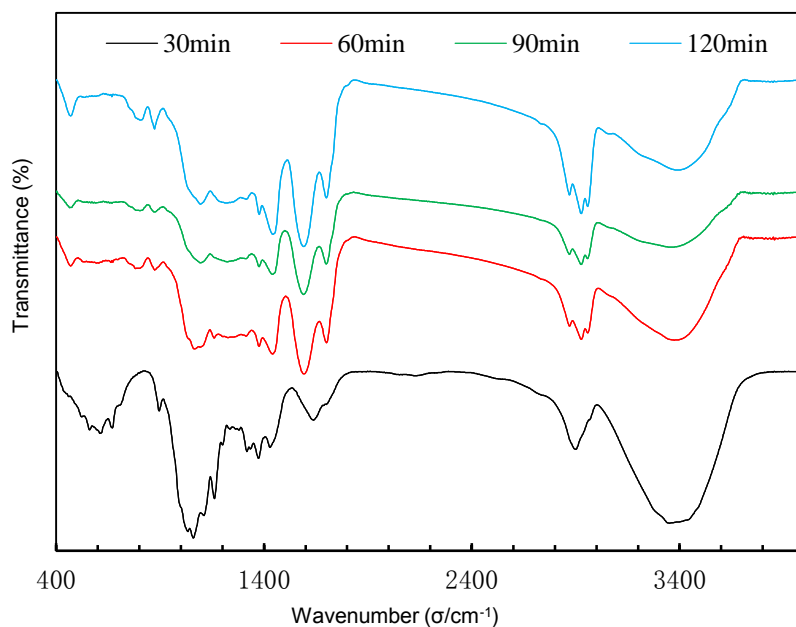

Fig. 3. FT-IR analysis of BIO-OIL obtained from cornstalk cellulose liquefaction in 160 mL ethanol at 320 °C

The weakening of the characteristic absorption at 1160 cm^{-1} (-C-O-C-) shows that cellulose became deeply decomposed after 60 min. As the reaction time increased, the absorption at 1660 cm^{-1} (-C=O) was enhanced, indicating that esters, ketones, and aldehydes were formed. Additionally, the absorption at 1710~1770 cm^{-1} (-COOH) was enhanced with increasing reaction time, which indicates an esterification reaction. The FT-IR results thus confirm the results given in Table 1. The absorption at 3360 cm^{-1} (-O-H) became weaker with increasing reaction time, indicating that acids and alcohols are converted (Sun *et al*. 2011).

Alcohol Solution-Esterification Mechanism

It can be concluded from Table 1 and Fig. 2 that one of the primary components of the bio-oil was esters. The yield of esters was 19.1% in 60 min when ethanol dosage was 160 mL. The major ester was ethyl lactate. The reactions occurring between cellulose were liquefaction and pyrolysis in sub- and supercritical ethanol. At the initial reaction stage, active cellulose is produced through cleavage (Wang *et al.* 2004). Free radicals, active cellulose cracking, ring-opening, aldol condensation, and dehydration form esters, ketones, and acids (Bicker *et al.* 2005; Tao *et al*. 2013), such as 2-hydroxy propionic acid and hydroxy ketone also can be involved. With increasing reaction time, more acids can undergo esterification, forming products such as 2-hydroxypropionate and ethyl-butyrate. Furthermore, esters are also produced by Baeyer-Villiger oxidization from cyclic ketones or aliphatic ketones (Berkessel *et al.* 2001; Yamada *et al*. 2007).
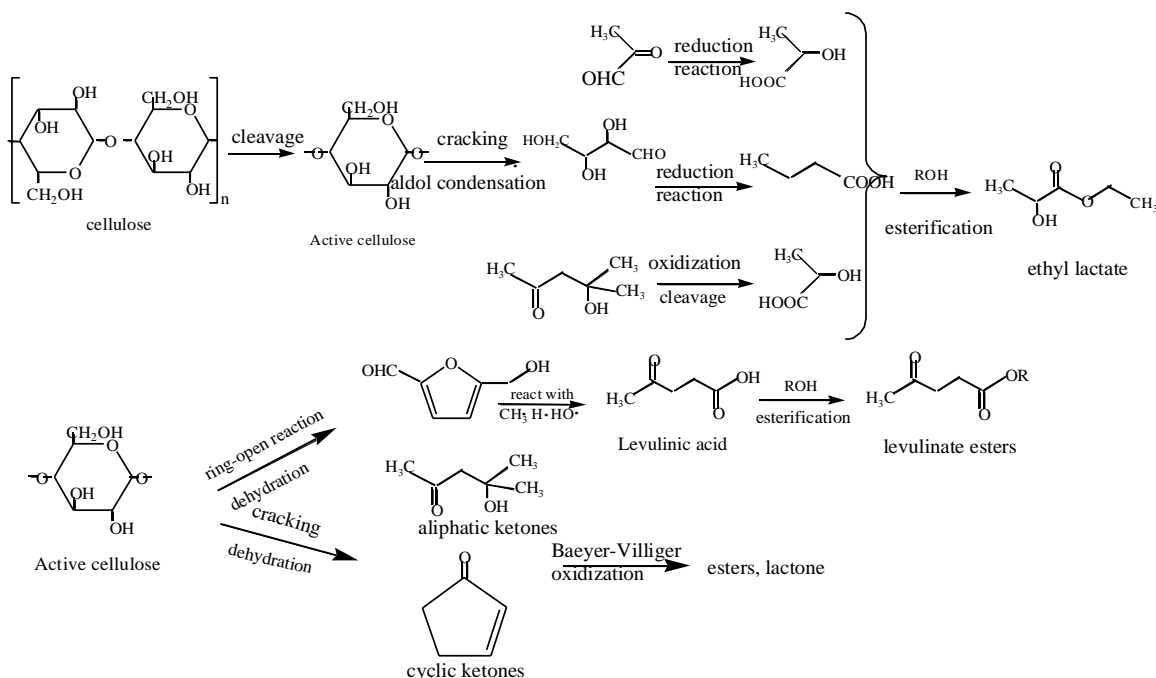
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Fig. 4. Pathways of esters formation

Pathways of Esters Formation with Reaction Time

In sub- and supercritical ethanol, at the initial reaction stage, active cellulose is produced through cleavage and dehydration of intramolecular and intermolecular hydrogen bonds present in cellulose. C_2 to C_5 acids, ketones, and intermediate free radicals are formed by degradation, dehydration, isomerization, and aldol condensation. Acids and ketones are converted to acids through decarboxylation and oxidation in the presence of hydrogen free radicals. Esters are synthesized by the esterification reaction between carboxylic acids and ethanol. Figure 5 shows the effect of reaction time on the pathways of esters formation.
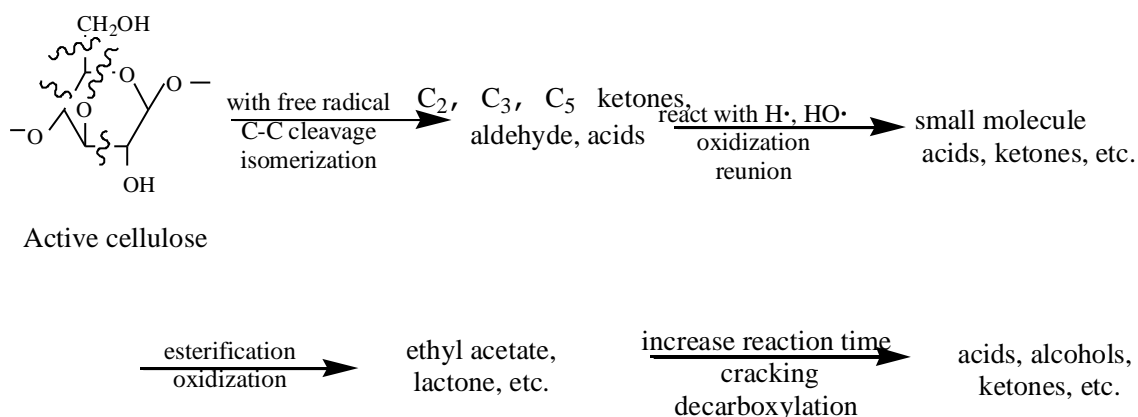

Fig. 5. Effect of reaction time on the pathways of esters formation

Reaction Network of Esters Formation

In sub- and supercritical ethanol, cellulose is converted to many kinds of esters containing $CH_3\cdot$, $CH_3CH_2\cdot$, and $HO\cdot$ through dehydration, cleavage, and aldol-condensation. The reason may be that ethanol free radicals participate in cellulose

liquefaction (Huang *et al.* 2011; Liu *et al.* 2012). A series of esters formation pathways is shown in Fig. 6.
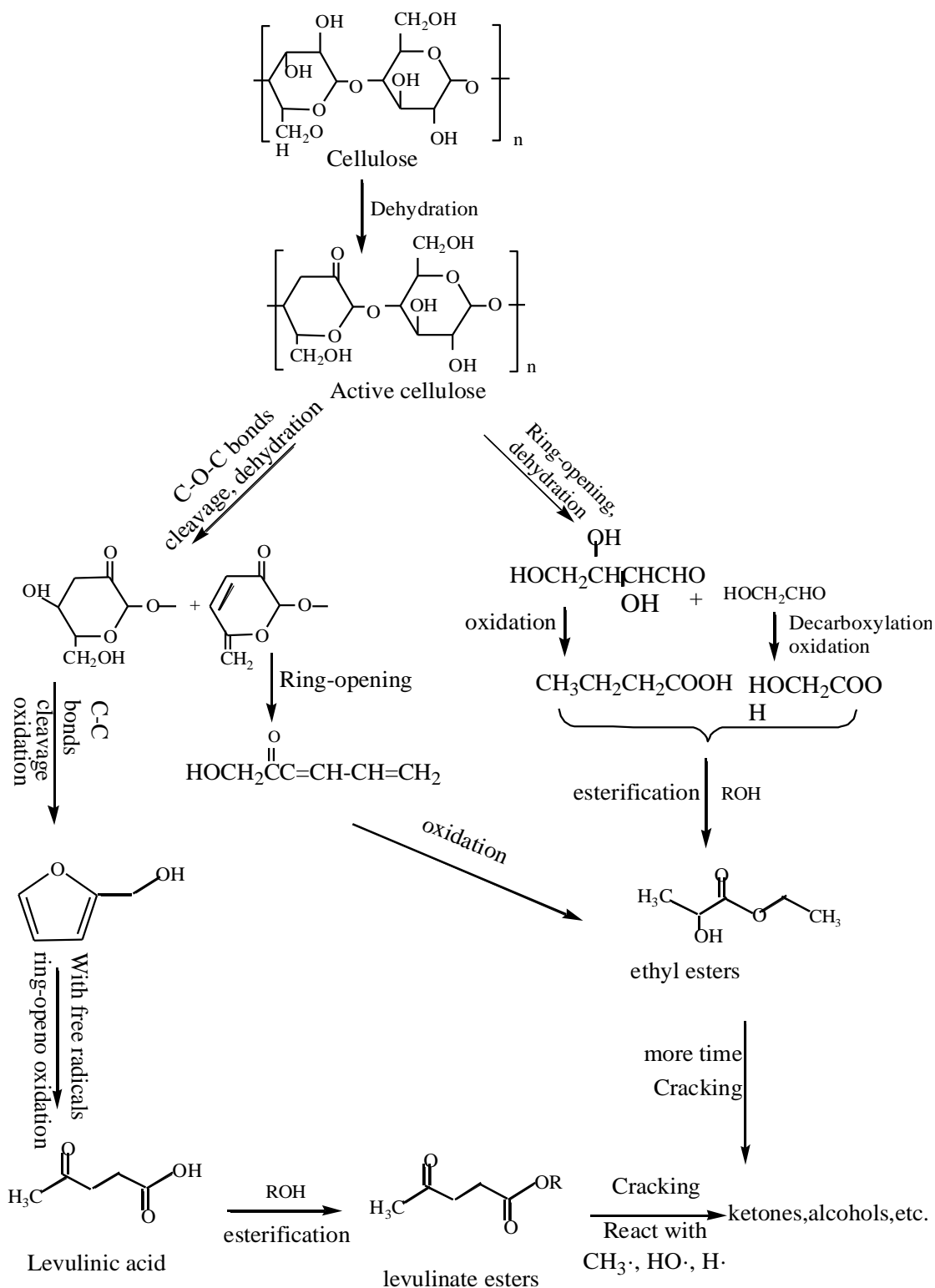

Fig. 6. Reaction network of esters formation from cellulose liquefaction

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CONCLUSIONS

1. Cellulose was liquefied in sub- and supercritical ethanol. The yield of bio-oil increased from 16.07% to 51.42% when the reaction time was increased from 0 min to 120 min.

2. The yield of esters rapidly increased from 10.0% to 19.1% with increasing reaction time from 30 to 60 min and then decreased with further increasing reaction time.

3. The formation of esters was affected by the reaction time in sub- and supercritical ethanol. In the cellulose liquefaction process, cellulose was converted to active cellulose at the initial stage and then formed esters such as ethyl lactate by ring-opening, dehydration, oxidization, and esterification.

4. Esters were decomposed to acids, alcohols, and other compounds with increasing reaction time in the presence of ethanol free radicals.

ACKNOWLEDGEMENTS

REFERENCES CITED

Berkessel, A., and Andreae, M. R. M. (2001). "Efficient catalytic methods for the Baeyer-Villiger oxidation and epoxidation with hydrogen peroxide," *Tetrahedron Letters* 42(12), 2293-2295.

Bicker, M., Endres, S., Ott, L., and Vogel, H. (2005). "Catalytical conversion of carbohydrates in subcritical water: A new chemical process for lactic acid production," *Journal of Molecular Catalysis A: Chemical* 239(1-2), 151-157.

Chumpoo, J., and Prasassarakich, P. (2010). "Bio-oil from hydro-liquefaction of bagasse in supercritical ethanol," *Energy & Fuels* 24, 2071-2077.

Huang, H. J., Yuan, X. Z., Zeng, G. M., Wang, J. Y., Li, H., Zhou, C. F., Pei, X. K., You, Q., and Chen, L. (2011). "Thermochemical liquefaction characteristics of microalgae in sub- and supercritical ethanol," *Fuel Processing Technology* 92(1), 147-153.

Li, C. S., and Suzuki, K. (2009). "Tar property, analysis, reforming mechanism and model for biomass gasification: An overview," *Renewable and Sustainable Energy Reviews* 13(3), 594-604.

Li, J., Kazakov, A., and Dryer, F. L. (2004). "Experimental and numerical studies of ethanol decomposition reactions," *J. Physical Chemistry A* 108(38), 7671-7680.

Li, H., Yuan, X., Zeng, G., Tong, J. Y., Yan, Y., Cao, H. T., Wang, L. H., Cheng, M. Y., Zhang, J. C., and Yang, D. (2009). "Liquefaction of rice straw in sub- and supercritical 1,4-dioxane–water mixture," *Fuel Processing Technol.* 90(5), 657-663.

Liu, H. M, Xie, X. A., Ren, J. L., and Sun, R. C. (2012). "8-Lump reaction pathways of cornstalk liquefaction in sub- and super-critical ethanol," *Industrial Crops and Products* 35, 250-256.

Luo, Z. Y., Wang, S. R., Liao, Y. F., Zhou, J. S., Gu, Y. L., and Cen, K. F. (2004). "Research on biomass fast pyrolysis for liquid fuel," *Biomass Bioenergy* 26(4), 55-62.

Mao, R., Zhao, Q., Dima, G., and Petraccone, D. (2010). "New process for the acid-catalyzed conversion of cellulosic biomass (AC3B) into alkyl levulinates and other esters using a unique one-pot system of reaction and product extraction," *Catalysis Letters* 141(2), 271-276.

Rataboul, F., and Essayem, N. (2011). "Cellulose reactivity in supercritical methanol in the presence of solid acid catalysts: Direct synthesis of methyl-levulinate," *Industrial & Engineering Chemistry Research* 50(2), 799-805.

Levine, R. B., Pennarat, T., and Savage, P. E. (2010). "Biodiesel production from wet algal biomass through in situ lipid hydrolysis and supercritical transesterification," *Energy & Fuels* 24(9), 5235-5243.

Poudel, J., and Oh, S. C. (2012). "A kinetic analysis of wood degradation in supercritical alcohols," *Industrial & Engineering Chemistry Research* 51(12), 4509-4514.

Sun, P. Q., Heng, M. X., Sun, S. H., and Chen, J. W. (2011). "Analysis of liquid and solid products from liquefaction of paulownia," *Energy Conversion and Management* 52(2), 924-933.

Tang, S. R., Lu, Y., Zhou, L., Xia, C. J., Wei, X. Y., and Zong, Z. M. (2009). "Analysis of depolymerization product of cornstalk in supercritical ethanol," *Journal of Anhui Agricultural Science* 37(11), 4869-4870.

Tao, H. X., Xie, X. A., Tang, C. Z., and Tian, W. G. (2013). "Mechanism of ketones formation from cellulose liquefaction in sub- and supercritical ethanol," *Journal of Fuel Chemistry and Technology* 41(1), 60-66.

Wang, G., Li, W., Li, B. Q., Chen, H. K., and Bai, J. (2007). "Direct liquefaction of sawdust under syngas with and without catalyst," *Chemical Engineering and Processing* 46(3), 187-192.

Wang, S. R., Luo, Z. Y., Tan, H., Hong, J., Dong, L. J., Feng, M. X., Cen, K. F. (2004). "The analyses of characteristics from biomass by flash of bio-oil produced pyrolysis," *Journal of Engineering Thermophysics* 25(6), 1049-1052.

Williams, P. T., and Onwudili, J. (2006). "Subcritical and supercritical water gasification of cellulose, starch, glucose, and biomass waste," *Energy & Fuels* 20(3), 1259-1265.

Yamada, T., Aratani, M., Kubo, S., and Ono, H. (2007). "Chemical analysis of the product in acid-catalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate," *Journal of Wood Science* 53(6), 487-493.

Yanik, J., Kornmayer, C., Saglam, M., and Mithat, Y. (2007). "Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products," *Fuel Processing Technology* 88(10), 942-947.

Zheng, C. Y., Xie, X. A., Tao, H. X., Zheng, L. S., and Li, Y. (2012). "Depolymerization of stalk cellulose during its liquefaction in sub- and supercritical ethanol," *Journal of Fuel Chemistry and Technology* 40(5), 526-532.

Zheng, C. Y., Xie, X. A., and Tao, H. X. (2013). "Distribution and characterizations of liquefaction of celluloses in sub- and super-critical ethanol," *BioResources* 8(1), 648-662.