EFFECT OF ACID CATALYSTS AND ACCELERATED AGING ON THE REACTION OF METHANOL WITH HYDROXY-ACETALDEHYDE IN BIO-OIL

Priyanka Bhattacharya, El Barbary Hassan, Philip Steele, Jerome Cooper,
and Leonard Ingram*

Bio-oil is a promising alternative source of energy produced from fast pyrolysis of biomass. Increasing the viscosity of bio-oil during storage is a major problem that can be controlled by the addition of methanol or other alcohols. This paper reports the results of our investigation of the reactions of short chain alcohols with aldehydes and acids in bio-oil. The reaction of methanol with hydroxyacetaldehyde (HA) to form the acetal was catalyzed by the addition of 7×10^{-4} M strong acids such as sulfuric, hydrochloric, p-toluene sulfonic acid, and methanesulfonic acid. HA formed 2,2-dimethoxyethanol (DME), and at 60 ^{o}C the equilibrium was reached in less than one hour. Smaller amounts of DME were formed in the absence of strong acid. HA, acetaldehyde, and propanal formed their corresponding acetals when reacted with methanol, ethanol, 1-propanol or 1-butanol. Esters of acetic acid and hydroxyacetic acid were observed from reactions with these same four alcohols. Other acetals and esters were observed by GC/MS analysis of the reaction products. The results from accelerated aging experiments at 90 ^{o}C suggest that the presence of methanol slows polymerization by formation of acetals and esters from low molecular weight aldehydes and organic acids.

Keywords: Bio-oil; Hydroxyacetaldehyde; Acetals; Esters; Stability

*Contact information: Department of Forest Products, Mississippi State University, Mississippi State MS 397620-9820. *Corresponding author: lingram@cfr.msstate.edu*

INTRODUCTION

The fast pyrolysis of lignocellulosic material can produce a liquid fraction called bio-oil, a gaseous fraction (10-30%), and char (10-20%). Bio-oil is the condensed liquid fraction, which is composed of different organic molecules e.g., aldehydes and ketones (15-35%), organic acids (15-35%), and phenolic compounds (6-15%), etc., which generally form due to the depolymerisation of the cellulose, hemicellulose, and lignin. Water is a major component of bio-oil and represents about 25% of its total composition (Bridgewater et al. 1999; Mohan et al. 2006; Bhattacharya et al. 2009). Also, bio-oil contains many of the organic compounds that are transient products and not true thermodynamic products at equilibrium. Due to the unexpended chemical potential, the kinetic products have a propensity to continue reacting after the bio-oil is cooled and stored (Bridgewater and Peacock, 2000; Bridgewater 2003)

The bio-oil primarily contains reactive hydroxyl, carbonyl, and carboxylic acid compounds that undergo etherification and esterification reactions during storage (Doshi et al. 2005; Zhang et al. 2007). These condensation reactions generally increase the molecular weight and viscosity of the bio-oil. The problem of polymerization of the bio-oil can be minimized if these reactions are controlled (Czernik et al. 1994, 2004). These researchers proposed that polymerization reactions can be stopped by reacting some small, monofunctional alcohols with the reactive sites of the oligomers present in the bio-oil. These reactions will terminate the chain and increase the stability of the bio-oil. Monofunctional alcohols, such as methanol and ethanol, can react with the acidic compounds present in the bio-oil and form polyesters, which may again undergo transesterification reactions with methanol to form low molecular weight materials. Similarly, aldehydes and ketones can be converted to the corresponding acetals and ketals by reacting with alcohols (Diebold and Czernik 1997). The use of small amount of mineral acid catalyst is important during these reactions. Sulphuric acid can be used as an acid catalyst for these types of reactions (Radlein et al. 1996).

Diebold and Czernik (1997) described condensation reactions of bio-oil with methanol. Methanol can form methyl acetate, methyl formate, methylal, acetal, etc., when reacting with the acetic acid, formic acid, formaldehyde, acetaldehyde, and hydroxyacetaldehyde present in the bio-oil. Addition of methanol can adjust the viscosity without affecting the LHV. It was found that the addition of 5% methanol decreased the aging rate from 2.5 cP/h to only 0.5 cP/hour without any noticeable change in the aging rate with increasing water content from 20 to 30%. Increasing the amount of methanol (10%) again lowered the aging rate but, it was much less pronounced compared to the 5% methanol addition. This decrease of aging rate can be explained by chemical reactions as described above. Therefore, the aging rate may depend on the molar amounts of additives added. Diebold and Czernik (1997) noted that the addition of 5 and 10 wt% methanol per 1000g of solution was effective in decreasing the aging rate. Ethylacetate and acetones were also found to reduce the viscosity (Czernik and Diebold 1997). The GC/MS analysis of the methanol added bio-oil indicated the decrease of hydroxyacetaldehyde, furfural, propenal, and acetic acid, etc. NMR analysis of the oil indicated the presence of ether and ester linkage (Diebold 2002).

Boucher et al. (2000a) also did similar experiments with methanol to see the effect on the viscosity of the bio-oil. The oil/aqueous phase/methanol mixtures were also studied in different ratios, 5% methanol/5% aqueous phase, 5% methanol/10% aqueous phase, 15% methanol /5% aqueous phase, and 15% methanol/10% aqueous phase. The viscosity of these solutions was definitely lower than that of the raw bio-oil, but the viscosity depended mostly on the amount of methanol present in the oil/methanol/aqueous phase. The higher the methanol concentration in the mixture, the lower was the viscosity.

The addition of methanol (70 wt %) during the catalytic conversion of bio-oil to hydrocarbons was found to be beneficial. The deposition of pyrolytic lignin within and outside the solid catalyst, or coking, was reduced, thus increasing the viability of hydrocarbon production (Gayubo et al. 2009).

Metal ions associated with particles of char contribute the continued reactivity of bio-oil during storage. Na, K, and Ca ions are believed to have the most negative effect. Vacuum pyrolysis produced a stable bio-oil with a combined concentration of Na, K, and Ca less than 21 ppm. Bio-oil produced by this process is stable over long periods of time

(Boucher et al. 2000b). Hot gas filtration of bio-oil vapors prior to condensation is another method that has been used to lower the inorganic ion content in bio-oil. Ash content was less than 0.01 percent, and the alkali metal content was less that 10 ppm. Bio-oil produced by this process had improved combustion characteristics and stability during storage (Czernik et al. 2002).

The reactions of aldehydes are of major interest in stability studies. The effect of the chemical structure on acetal formation for a wide range of alcohols and aldehydes was reported by Minne and Adkins (1933). Reactions were carried out at 25 °C with HCl catalyst, and the concentration of the unreacted aldlehyde was determined by titration with sodium sulfite. The ratio of the number of moles of alcohol to moles of aldehyde was usually 11 to 1, and the time required for the reaction to reach equilibrium ranged from a few hours to a few days. K_{eq} (Equation 1) was calculated on a mole fraction basis and varied among alcohols and aldehydes. The increase in chain length of the alcohol did not produce a consistent trend in the change in equilibrium constant.

$$K_{eq} = \frac{[\text{acetal}][\text{water}]}{[\text{aldehyde}][\text{alcohol}]^2} \qquad (1)$$

Table 1 shows the range of equilibrium constants obtained for selected alcohols and aldehydes. Steric and structural characteristics have been proposed to be major factors affecting K_{eq}. Additional discussion of these results, as related to bio-oil, were published by Diebold (2002).

Table 1. Equilibrium Constants for Selected Aldehydes and Alcohols *

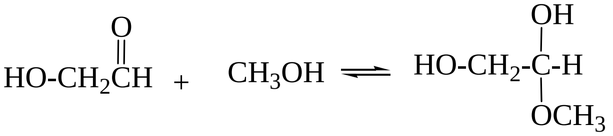
Alcohol	**Aldehyde**	**K_{eq}**
Methyl-	Acetaldehyde	2.41
Ethyl-	Acetaldehyde	1.21
n-Propyl-	Acetaldehyde	1.06
n-Butyl-	Acetaldehyde	3.08
Ethyl-	Hydroxyacetaldehyde	0.28
Methyl-	Furfural	0.114
Ethyl-	Furfural	0.041

* (Minne and Adkins 1933)

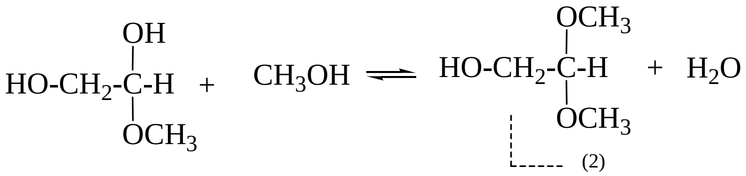
The reaction of an alcohol with an aldehyde to form an acetal can be shown in two steps: Reactions 2 and 3 show the formation of 2,2-dimethoxyethanol from hydroxyacetaldehyde and methanol. In Reaction 2 the hemiacetal is formed as an intermediate, which reacts with a second molecule of methanol to give the product.

The continued reactions of the components in bio-oil are a major nuisance with respect to fuel use. Flow and fluid transfer are slowed by the increase in viscosity, and pipes and storage tanks may become completely clogged during long-term storage.

The objective of this research was to investigate the reactions of short chain alcohols with the aldehydes and acids in bio-oil. A general hypothesis is that reaction of methanol with aldehydes plays a role in reducing the rate of viscosity increase during bio-oil storage. Since with respect to polymerization aldehydes are difunctional and most of the acids found in bio-oil are monofunctional, the reaction of methanol with hydroxyacetaldehyde to form 2,2-dimethoxyethanol was a primary interest.



$$\mathrm{HO\text{-}CH_2\overset{\overset{O}{\|}}{C}H} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{HO\text{-}CH_2\text{-}\overset{\overset{OH}{|}}{\underset{\underset{OCH_3}{|}}{C}}\text{-}H} \qquad (2)$$



$$\mathrm{HO\text{-}CH_2\text{-}\overset{\overset{OH}{|}}{\underset{\underset{OCH_3}{|}}{C}}\text{-}H} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{HO\text{-}CH_2\text{-}\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}\text{-}H} + \mathrm{H_2O} \qquad (3)$$

(2)

EXPERIMENTAL

Catalyst Evaluation

Bio-oil for these experiments was produced from pine feedstock using the 2 kg/hr auger reactor, located at the Department of Forest Products, Mississippi State University. The physical and chemical characteristics of bio-oil produced from pine feedstock were previously described (Ingram et al. 2008). Five different catalysts were tested for the reaction of bio-oil with methanol. The catalysts were *p*-toluenesulphonic acid, methanesulphonic acid, sulfuric acid, hydrochloric acid, and phosphoric acid. The weight of methanol and bio-oil for the experiments were 80 g and 1 g, respectively. A representative sample (5 ml) was placed in a screw cap test tube, and the reaction was carried out at 60 ^{o}C temperature in water bath with each catalyst at a concentration of 7 x 10^{-4} M. A test tube was removed from the water bath after 0.5, 1, 2, 2.5, and 3 h, and then the formation of 2,2-dimethoxyethanol (DME) from hydroxyacetaldehyde was monitored by gas chromatography/mass spectrometry (GC/MS) analysis. Similar experiments were performed with the filtered bio-oil to determine the effect of char removal.

Reactions of Bio-oil and Methanol with Different Weight Ratios

Bio-oil was reacted with methanol in different w/w ratio to identify the optimum bio-oil/methanol ratio. An excess of methanol methanol (80 g) was used with sample weights of bio-oil ranging from 0.05 g to 5 g. Also, lower ratios of methanol to bio-oil were used as follows: 95:5, 90:10, 80:20, 50:50, 20:80, 10:90, and 5:95. The reaction procedure and conditions were as previously described using sulfuric acid as the catalyst. The concentration of DME was determined by GC/MS analysis.

Reaction of Bio-oil and Other Alcohols

Pine bio-oil (1 g) was also reacted with excess (~80 g) ethanol, 1-propanol, and 1-butanol, respectively, in the presence of sulfuric acid catalyst. The reaction conditions were the same as those used with methanol. As soon as the reaction was completed, the samples were removed and cooled in the ice to stop further reactions. Products were identified by GC/MS analysis.

Accelerated Aging Tests

Accelerated aging tests were done at 90 ^{o}C with raw pine bio-oil and pine bio-oil mixed with different amounts of methanol (0%, 5%, 10% and 20%). Aging was done for 1, 2, 3, 4, and 5 days. The amount of DME was calculated by reacting the aged sample with the sulphuric acid catalyst in methanolic solution (7 x 10^{-4} molar concentration) at 60 ^{o}C in the water bath. The GC/MS procedure was the same as used for other experiments. The amount of hydroxyacetaldehyde was then calculated using the amount of DME formation.

Amount of HA (hydroxy acetaldehyde) = (60 X Amount of DME)/106

% HA = (Amount of HA / Wt of Bio-oil) X 100

The viscosities of each aged sample and the control sample were also measured at 40^{o}C, using a Rheotek flow-through viscometer.

An analysis-of-variance model determined the significance of time of aging on sample viscosity for each methanol concentration separately. Accelerated aging time was entered as the independent treatment variable while sample viscosity was measured and entered as the dependent response variable as shown in Equation 4. Three replicates were used for each treatment.

$$\text{Viscosity} = \mu + \text{Age} + \varepsilon \qquad (4)$$

where: µ represented the overall mean response; Age represented the numbered of days of aging and ε represented the error term.

GC/MS Analyses

Each sample was analyzed on a Clarus 500 Gas Chromatography Mass Spectrometer. Helium (2.0 ml/min) was the carrier gas. A 30 m x 0.32 mm internal diameter fused silica capillary column, coated with 5% phenyl methylpolysiloxane, was employed. The initial GC oven temperature was 40 ^{o}C (4 min) and it was raised at 5 ^{o}C/min to 280 ^{o}C (held for 15 min). The injector temperature was 270 ^{o}C. The mass spectrometer employed a 70 eV electron impact ionization mode and a source (detector) temperature of 210 ^{o}C. A calibration standard mixture of 2,2-dimethoxyethanol (Sigma-Aldrich) with an internal standard of diphenylmethane was used for the quantitative calculation. The concentration of DME in the calibration standard varied from 10 - 200 µg/ml and the concentration of DPM was 30 µg/ml. The average response factor over these concentration range was calculated using Equation 5,

$$R_f = (A_{DME} * C_{DPM}) / (A_{DPM} * C_{DME}) \qquad (5)$$

where, A_{DME} = Peak area of m/e 75, C_{DME} = Concentration of DME, and R_f = Response factor. R_f was then used to calculate the amount of DME in each sample.

RESULTS AND DISCUSSION

Catalysts Evaluation

The percentage of DME was calculated using the results from the GC/MS analysis and the weight of bio-oil in each sample. Figure 1 shows the results from the reaction of methanol and bio-oil with different catalysts. With strong acids the maximum concentration of DME occurred within about 1 hour. Phosphoric acid ($Ka_1 = 8 \text{ X } 10^{-3}$) and the acetic acid ($Ka_1 = 1.8 \text{ X } 10^{-5}$) only have a slight effect on the rate of formation of DME during this 3 hour experiment. (Acetic acid is present in pine bio-oil at concentrations of about 5-10 percent.)

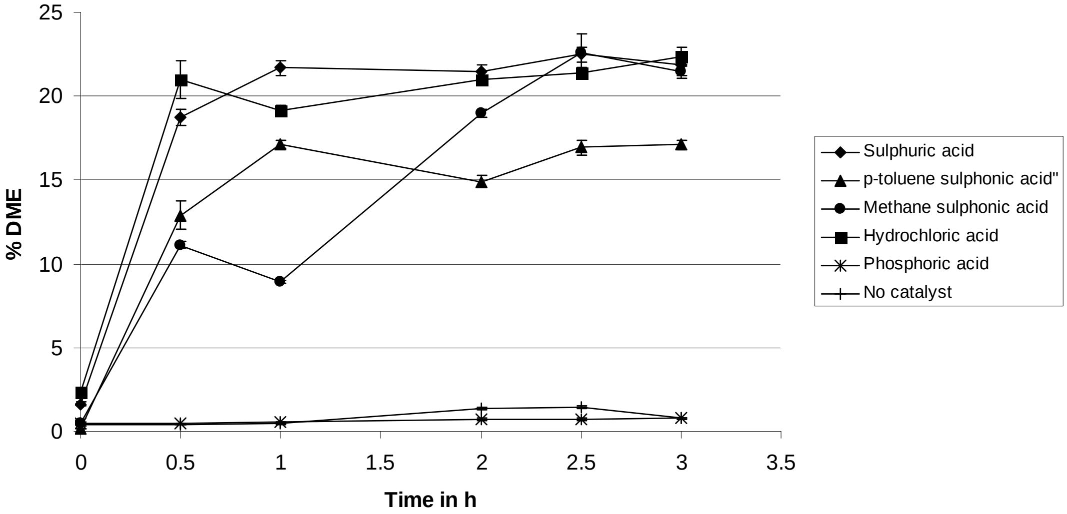


Figure 1. Effect of different catalysts in the formation of DME (using unfiltered bio-oil)

The same experiments were done with mixtures of methanol and bio-oil that had been filtered through 25 micron filter paper to remove the char. The amount of char in this bio-oil was approximately 0.2 percent. When strong acids were used as the catalyst, the DME reached the maximum concentration after about 1 hour. After char removal, there was no observable effect on the rate of DME formation with phosphoric acid or the residually occurring acetic acid. Apparently the char that is present in bio-oil has slight catalytic effect on the reaction of methanol and hydroxyacetaldehyde (Figs. 1 and 2). Based on the results from these experiments, sulfuric acid was chosen as the catalyst for other experiments.

Reaction of Bio-oil and Methanol with Different Weight Ratio

The percentage of DME was calculated from the results of experiments with different ratios of methanol to bio-oil (80 g to 0.05 g through 80 g to 5 g). A decrease in the amount DME formed was noted at about the 4:1 ratio. For N=8 measurements at higher ratios, the amount of DME was 24.8 percent, with a coefficient of variation of 10.6 percent based on the original weight of bio-oil. These results indicate that the precision of these measurements is adequate for the conclusions drawn. With weight ratios of methanol to bio-oil of 4:1 the yield of DME was near maximum (Fig. 3).

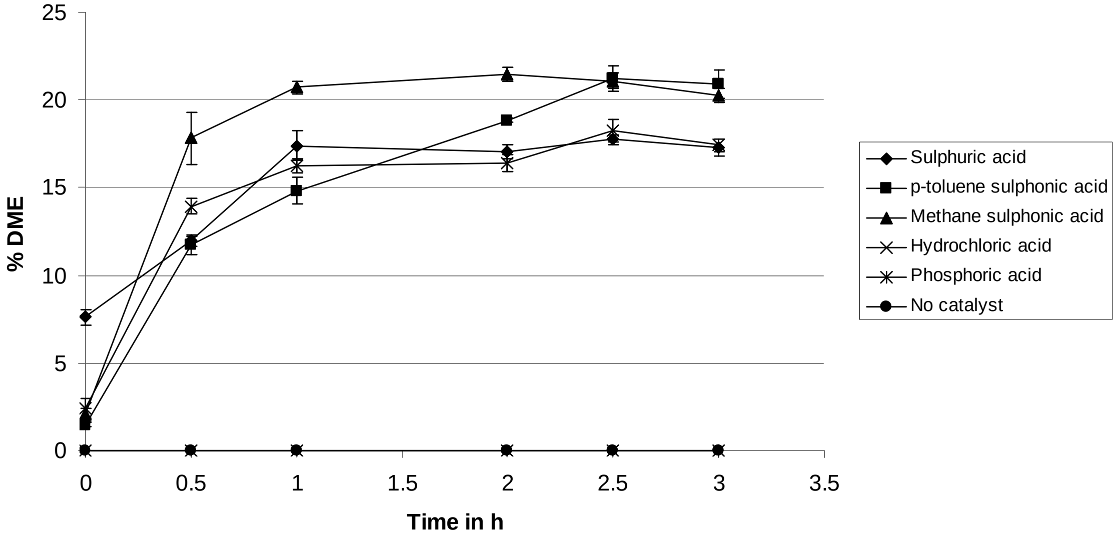


Figure 2. Effect of different catalysts on the formation of DME (using filtered bio-oil)

One difficulty in obtaining the maximum yield of DME under equilibrium conditions is attributed to the water content of the bio-oil used in these experiments (15 percent). Equations 2 and 3 show the reactions for the conversion of HA to DME. The presence of water in the starting materials requires an increased amount of methanol to drive the reaction to the completion.

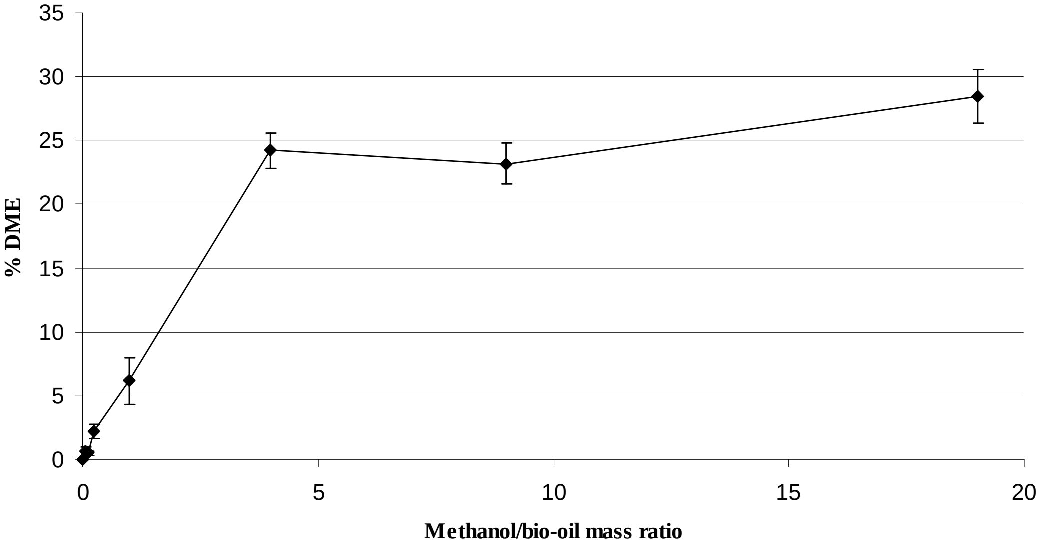


Figure 3. Percent DME from the reactions of bio-oil and methanol (different w/w ratios) with sulphuric acid catalysts

Reaction of Bio-oil with Other Alcohols

Tables 2 and 3 show the identification of acetals and esters when bio-oils were reacted with methanol, ethanol, 1-propanol, and 1-butanol. HA, acetaldehyde, and propanal formed their corresponding acetals when reacted with methanol, ethanol, 1-propanol or 1-butanol. Esters of acetic acid and hydroxyacetic acid were observed from reactions with these same four alcohols. Other acetals and esters were observed by GC/MS analysis of the reaction products.

Accelerated Aging Tests

With these experimental conditions bio-oil was reacted with methanol in two stages. In the first stage different amounts of methanol (0 to 20 %) were reacted at 90 °C without a catalyst for a period of 1 to 5 days. In the second stage excess methanol with a catalyst was reacted with methanol at 60 °C. The effect of these reaction conditions on the concentration of HA are shown in Table 4 and Fig. 4. The decrease in concentration of HA was log linear with time, indicating that the reaction was likely pseudo first order.

The decrease in concentration of HA was slowest in samples that contained 20 % methanol and highest in samples that did not contain methanol. Since the conditions of the second stage of the experiment were the same for all samples, the rate of decrease in the concentration of HA was slowed by in bio-oil samples that contained methanol. After five aging days at 90 °C, the lowest concentrations of HA was found in bio-oil samples that did not contain methanol.

Initial viscosity measurements on bio-oil samples containing 0, 5, 10, and 20 % methanol with no catalyst ranged from 5.66 to 3.76 cSt. The lowest viscosity occurred with samples that contained 20 % methanol (Table 5.) This decrease in viscosity is probably from dilution, since formation of DME or other reaction products were not observed to occur to a measurable extent with these same type samples from other experiments. After aging for 4 to 5 days at 90 °C, the initial effect of methanol on viscosity was diminished. The viscosity of samples containing 0 and 5 % methanol could not be determined due to thickening and coagulation of the samples. The viscosity of all samples increased with accelerated aging, but samples containing 10 or 20 % methanol had viscosities less that 7 cSt after the maximum aging time period of 5 days.

Table 2. Tentative Identification of Acetals by GC/MS Analysis

Aldehydes present in bio-oil		Acetals identified after the reaction		
	Methanol	Ethanol	1-Propanol	1-Butanol
Acetaldehyde	x	x	x	x
Hydroxyacetaldehyde	x	x	x	x
2-Hydroxypropanal	x	x		
2,3-Butanedione	x	x		
Methylglyoxal	x	x	x	
Formaldehyde	x	x	x	
Propanal	x	x	x	x
Heptanal	x	x		
Butanone	x	x		x

Table 3. Tentative Identification of Esters by GC/MS Analysis

Acids present in bio-oil	Esters identified after the reaction			
	Methanol	Ethanol	1-Propanol	1-Butanol
Acetic acid	x	x	x	x
Propanoic acid	x	x	x	x
Propionoic acid	x	x		x
Hydroxy acetic acid	x	x	x	x
Butanoic acid	x	x	x	x
2-Butenoicacid	x			
Nonanediooic acid	x	x		
Hexadecanoic acid	x	x		
10-Octadecenoic acid	x	x		

Table 4. Linear Regression Values for ln (concentration of HA) versus Time for 0, 5, 10, and 20 percent Methanol in Bio-oil Stored at 90 ^{o}C for Five Days

Percent Concentration of Methanol in Bio-Oil	Slope	Y Intercept	R^2
0	-0.87	2.48	0.98
5	-0.69	2.72	0.95
10	-0.62	2.78	0.98
20	-0.53	2.87	0.88

Table 5. Results of Accelerated Aging; Comparison-of-Means Tests by Methanol Concentration

Methanol conc. (%)	Accelerated aging time (day)											
	0		1		2		3		4		5	
	Mean	M. Test[b]	Mean	M. Test[b]	Mean	M. Test[b]	Mean	M. Test[b]	Mean	M. Test[b]	Mean	Means Test[b]
0	5.66	A	6.14	B	6.33	C	7.41	D	Not measured[a]		Not measured[a]	
5	5.29	A	5.39	A	5.78	B	6.36	C	Not measured[a]		Not measured[a]	
10	4.46	A	4.53	A	4.89	B	6.31	C	6.12	D	6.91	E
20	3.76	A	3.82	A	4.08	B	5.76	C	6.04	D	6.29	E

Samples were aged at 90^{o}C and viscosity was measured in cSt.

[a] The samples were very viscous and two separate layers were formed after 4 days aging.

[b] Means test: capital letters indicate results of comparison-of-means tests. Values with the same letter did not differ significantly at the 0.05 level.

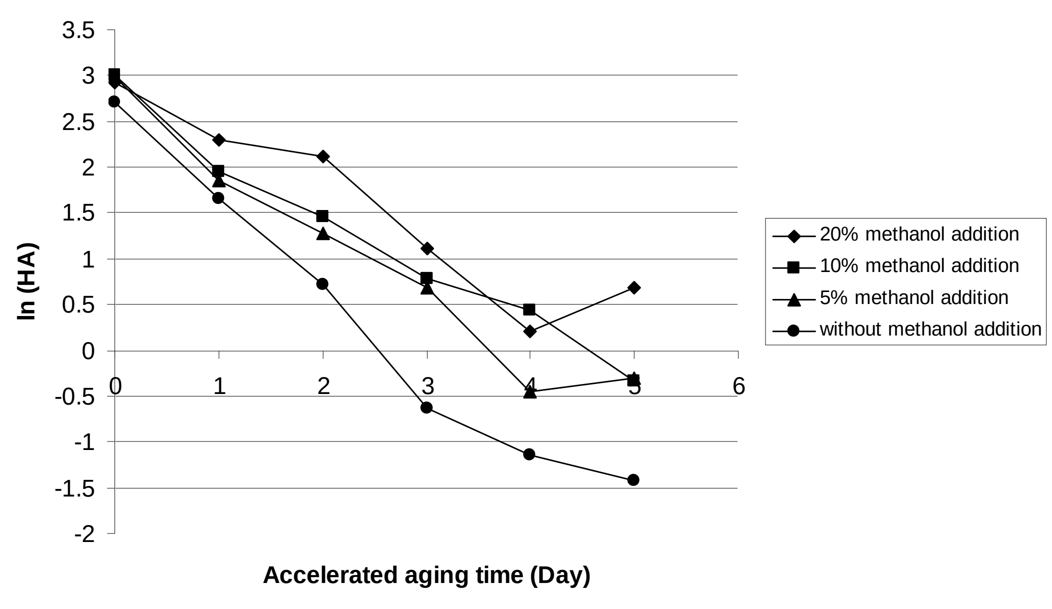


Figure 4. Effect of methanol on concentration of hydroxyacetaldehyde during 5 days aging of bio-oil at 90 °C

CONCLUSIONS

Strong acids such as sulfuric, hydrochloric, PTSA, and MSA decreased the time for the formation of DME from methanol and HA to reach maximum concentration. This reaction is apparently at equilibrium, since no apparent change in concentration of DME occurred after about 1 to 2 hours. Weak acids such as phosphoric and acetic (already present in bio-oil) had little or no effect on the reaction rate. The presence of char in bio-oil had a slight effect on the formation of DME from the reaction of methanol and hydroxyaldehyde when no strong acid catalyst was present.

With five day accelerated aging of bio-oil, the results indicated that the addition of methanol to bio-oil slows, but does not stop, the decrease in concentration of HA. This result suggests that the reactivity of HA and other aldehydes in bio-oil may contribute to the increase in viscosity during storage. The increase in molecular weight and increase in viscosity were slowed in accelerated aging tests when similar amounts of methanol were added to bio-oil. The formation of other esters and acetals were observed by GC/MS analysis when bio oil was reacted with other primary alcohols and sulfuric acid catalyst.

REFERENCES CITED

Bhattacharya, P., Steele, P. H., Hassan, E. B. M., Mitchell, B., Ingram, L., and Pittman, C. U. (2009). "Wood/plastic copyrolysis in an auger reactor: Chemical and physical analysis of the products," *Fuel* 88(7), 1251-1260.

Boucher, M. E., Chaala, A., and Roy, C. (2000a). "Bio-oils obtained by vacuum pyrolysis of soft wood bark as a fuel for turbine engines. Part 1: Properties of bio-oils and its blend with methanol and pyrolytic aqueous phase," *Biomass and Bioenergy* 19(5), 337-350.

Boucher, M. E., Chaala, A., Pakdel, H., and Roy, C. (2000b). "Bio-oils obtained by vacuum pyrolysis of soft wood bark as a liquid fuel for gas turbine. Part II: Stability and ageing of bio-oil and its blend with methanol and pyrolytic aqueous phase," *Biomass and Bioenergy* 19(5), 351-361.

Bridgwater, A., Czernik, C., Diebold, J., Meier, D., Oasmaa, A., Peacocke, C., Piskorz,J., and Radlein, D. (1999). "An introduction to fast pyrolysis of biomass for fuels and chemicals," *Fast Pyrolysis of Biomass: A Handbook.* CPL Scientific Publishing Services Limited: 43 Kingfisher Court Newbury RG14 5SJ UK, Pp. 1-13.

Bridgwater, A. V., and Peacock, G. V. C (2000). "Fast pyrolysis process for biomass," *Renewable and Sustainable Energy Reviews* 4(1), 1-73.

Bridgwater, A. V. (2003). "Renewable fuels and chemicals by thermal processing of biomass," *Chemical Engineering Journal* 91(2-3), 87-102.

Czernik, S., Johnson, D. K., and Black, S. (1994). "Stability of wood fast pyrolysis oil," *Biomass and Bioenergy* 7(1-6), 187-192.

Czernik, S., Maggi R., and Peacocke, G. V. C. (2002). "Review of methods for upgrading biomass-derived fast pyrolysis oils," in Bridgwater, A. V. (ed.), *Fast Pyrolysis of Biomass: A Handbook*, Volume 2; CPL Press, Liberty House: The Enterprise Centre, New Greenhap Park, Newbury RG19 6HW, pp 131 to145.

Czernik, S., Bridgewater, A. V. (2004). "Overview of applications of biomass fast pyrolysis oil," *Energy and Fuels* 18, 590-598.

Diebold, J. P., and Czernik, S. (1997). "Additives to lower and stabilize the viscosity of pyrolysis oils during storage," *Energy and Fuel* 11, 1081-1091.

Diebold, J. P. (2002). "A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils," in Bridgwater, A. V. (ed.). *Fast Pyrolysis of Biomass: A Handbook*, Volume 2; CPL Press, Liberty House: The Enterprise Centre, New Greenhap Park, Newbury RG19 6HW, UK. pp 243-292.

Doshi, V. A., Vuthaluru, H. B., and Bastow, T. (2005). "Investigations into the control of odour and viscosity of biomass oil derived from pyrolysis of sewage sludge," *Fuel Processing Technology* 86, 885-897.

Gayubo, A. G., Valle, B., Aguayo, A. T., Olazar, M., Bilbao, J. (2009). "Attenuation of catalyst deactivation by cofeeding methanol for enhancing the valorization of crude bio-oil," *Energy and Fuels* 23, 4129-4136.

Ingram, L., Mohan, D., Bricka, M., Steele, P., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., and Pittman, C. U. (2008). " Pyrolysis of wood and bark in auger reactor: Physical properties and chemical analysis of the produced bio-oils," *Energy and Fuels* 22 (1), 614-625.

Minne, N., and Adkins, H. (1933). "Structure of reactants and the extent of acetal formation," *Journal of American Chemical Society* 55, 299-309.

Mohan, D., Pittman, C. U., and Steele, P. (2006). "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy and Fuels* 20, 848-889.

Radlein, A.G., Piskorz, J. K., and Majerski, P. A. (1996). "Methods of upgrading biomass pyrolysis liquids for use as fuels and as a source of chemicals by reaction with alcohols," Application for Canadian patent. Int Cl. C10L 1/02; C07G 17/00.

Zhang, Q., Chang, J., Wang, T., and Xu, Y. (2007). "Review of biomass pyrolysis oil properties and upgrading research," *Energy Conversion and Management* 48, 87-92.

Article submitted: Sept. 21, 2009; Peer review completed: Jan. 28, 2010; Revised version received and accepted: March 8, 2010; Published: March 10, 2010.