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Characterization of Phase Separation and Upgrading of Hardwood Derived Bio-oil using Alcoholic Solvents**

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ARTICLE INFO

Article history:
Received 31 May 2020
Received in revised form
09 October 2020
Accepted 29 October 2020

Keywords:
Bio-oil
Bio-oil aging
Bio-oil upgrading
Pyrolysis

ABSTRACT

Bio-oil produced by fast pyrolysis of hardwood was studied. It was observed that bio-oil was phase separated after 15 hours during accelerated aging at 80 ºC and the proportion of the viscous bottom phase continued to gradually increase with prolong aging. The chemical compositions of each phases proved that phase separation of bio-oil is not an effective tool to segregate undesired components into a single phase. GC-MS analysis shows that, during accelerated aging, some phenolic, sugar, ketone, ester, acid, furans and aldehyde components are disappearing from the bio-oil and these components might undergo polymerization or condensation reactions with the heavy pyrolytic fraction of bio-oil. The addition of solvents greatly retards phase separation. Amongst the various alcohols tested (isopropanol, ethanol, propanol and butanol), isopropanol is the most effective in retarding phase separation. These polar solvents change the chemical composition by reactions such as esterification. Addition of 10 % of isopropanol prevents the phase separation for 13 days at 80°C.

1. INTRODUCTION

Pyrolysis is a thermochemical process that converts solid biomass into a liquid fuel, which is called bio-oil [1]. In pyrolysis, biomass is heated to a temperature around 450-550 ºC in the absence of oxygen and the residence time of vapor is kept very low (about 0.5 – 5.0 s) and the condensable part of the vapor is condensed to get the liquid bio-oil. Conversion of biomass into bio-oil is one of the most promising methods to replace depleting fossil fuel resources with renewable feedstock. At room temperature, bio-oil is often, initially, a single phase, dark, viscous liquid that contains more than 300 chemical components [1]-[4].

Bio-oil has several undesired properties such as high viscosity, high acidity, instability due to ongoing chemical reactions and phase separation and change in viscosity upon ongoing storage time (which is called aging) [1]-[4]. At the same time, if pyrolysis bio-oil is to be used as a liquid fuel, the high oxygen (typically 45-50 wt%) and water contents (typically 15-30 wt%) and resulting lower energy density than conventional fuel oils are also amongst the deleterious properties [5], [6]. Therefore, bio-oil needs further stabilization and upgrading before it can be used as a fuel in existing engines [1].

According to Batts and Fathoni [7], the term “fuel stability” characterizes the general resistance of a fuel to change. At ambient conditions, it can refer to “storage stability”, that is, the ability of a fuel to remain in storage over an extended period of time without appreciable deterioration. Most of the previous studies, have studied the absolute increase in bio-oil viscosity [2]-[4] or water content [7] or molecular weight [1]-[4], [8] during storage as instability measures. The average molecular weight increases due to ongoing polymerization reactions between bio-oil components during storage [4]-[9]. However, increases in pH or Total Acid Number (TAN) are barely noticeable during aging [3], [9] and hence, they are not good indicators for the measurement of the stability or degree of aging of bio-oil [10].

The literature [1]-[4] indicates that the whole picture of fuel stability is very complex and that there is likely no single explanation for all the phenomena associated with bio-oil degradation. It has been observed during aging that different unsaturated and reactive components interact by means of polymerization, esterification, acetalization, oxidization or dimerization to form larger molecules and consequently cause changes in physical properties, such as viscosity [1]-[4]. To prevent these undesired aging reactions, physical and chemical upgrading methods have been investigated. They include solvent addition [11]-[18], emulsification with diesel fuel [19]-[23], deoxygenation using zeolite catalysts and catalytic hydrotreating.

Hydrotreating is considered to be a very expensive and energy consuming process. It also reportedly causes

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**This paper was presented at the *ICUE 2020 International Conference on Energy, Environment, and Climate Change* held at the Asian Institute of Technology, Pathumthani, Thailand from 20-22 October 2020.

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phase separation [24] and drastically increases the viscosity of the organic phase [1]. Deoxygenation processes based on catalytic hydrotreatment or catalytic cracking not only significantly reduce the liquid yield, but are also capital intensive [5]. Only a very small fraction of bio-oil is soluble in typical diesel fuels [1]. However, recently, many efforts have been directed to producing an emulsion of bio-oil with diesel [19]-[23]. In most cases, there is an immediate phase separation between the bio-oil and diesel and, therefore, an emulsifying agent needs to be added at high concentration [19]-[23] to stabilize the emulsion, resulting in a high fuel cost [19]. Udomsap *et al.* [23] report that up to 40% of surfactant needs to be added to emulsify bio-oil with oil with a proportion of 40%. Even with alcohols, a very high concentration of alcohol is required for proper emulsification [20].

Additives, especially, low viscosity alcohols, can reduce both the initial viscosity of bio-oil and mitigate its increase during aging [2], [3], [25], [26]. Ethyl Acetate, acetone, methanol, ethanol and isopropanol are the additives that were the most commonly used in previous studies [1]-[4], [25]. As it was found by Diebold and Czernik [2], the effect of the solvents on viscosity reduction was greater than would be expected from physical dilution. This suggests that beneficial chemical reactions occur between bio-oil and solvent [1].

Oasmaa [27] developed the concentration method, which removes part of the water and light volatiles and replaces them with alcohols can improve the quality (viscosity, flash point and stability) of bio-oil. In this case, a fraction of the carboxylic acids, aldehydes and ketones are removed along with water. Zuo-gang *et al.* [28] also improved the quality of bio-oil by removing acid compounds from the bio-oil by molecular distillation. Fractional condensation has also been experimented in producing a more stable bio-oil [29], [30].

As a result of ongoing chemical reactions, polymerization processes, and initial high water concentrations, during prolong storage, bio-oil spontaneously separates into two phases, i.e., an aqueous top phase with high concentration of water and water soluble compounds, and a viscous bottom phase, which consists of lignin extractives [2], [31], [32]. Because of the phase separation, bio-oil will not only create problems in storage, transportation and upgrading, but also make it no longer be able to use as a fuel in real application. Therefore, phase separation is considered as one of the major issues which require more research attention into.

A few studies on bio-oil phase separation has been done in the past. The studies have been conducted separately for upper and bottom phases of bio-oil layers after phase separation by gravity or by centrifugation [32]. Some work has also been done to extract valuable chemical and fuels from bio-oil by effective phase separation through salt addition [31], [33]. Scholez *et al.* [34], [35] induced phase separation through water extraction, adding bio-oil to cold water, to extract pyrolytic lignin from bio-oil. Since the water insoluble fraction is high in phenolics compounds, Xu *et al.* [36] investigated the possibility of using this fraction of rice husk bio-oil for the production of novolac resins. Boucher *et al.* [37] have shown that adding methanol is useful for delaying the phase separation of vacuum pyrolysis softwood bark bio-oil. However, most of the recent upgrading studies use a high concentration of solvent, reaching more than 50 % of the mixture [11] – [15].

Therefore, the objective of this research is to analyze the phase separation behavior and characterize the ongoing chemical changes during aging of fast pyrolysis bio-oil from hardwood and to identify the solvents and additives that are effective at retarding phase separation.

2. MATERIALS AND METHODS

2.1 Chemicals and Materials

Fast pyrolysis bio-oil was purchased from the Biomass Technology Group (BTG), The Netherlands. Bio-oil is a single-phase liquid at room temperature, with 21.8 wt% water content. butanol, ethanol, isopropanol and propanol were purchased from the Sigma Aldrich Company.

2.2 Quantification of Phase Separation due to Aging of Bio-oil

A set of pre-weighed bio-oil samples (10g) was sealed in glass tubes and kept at 80°C in a constant temperature water bath for different periods of time. At hourly intervals, one sample was taken out of the bath, cooled down to room temperature and the weight of the aged bio-oil was measured to determine the weight of volatile losses during aging. In each case, the weight loss of the aged bio-oil was less than 2.0 wt%. Then, the samples were centrifuged in a Marathon 2100 centrifuge (Fisher Scientific) for 20 minutes at 5000 rpm and checked for phase separation. Once the first signs of phase separation appeared, the sealed sample was stored at 4°C in a refrigerated cabinet for 20 hours. After 20 hours, the top and bottom phases were separated by decanting and each phase was weighed. The water content of the top and bottom phases was measured using a Mettler Toledo volumetric Karl Fischer titrator using AquaStar CombiSolventKeto as the titrant. The higher heating value (HHV) of both top and bottom phases was measured using a bomb calorimeter (IKA C200). The same steps were followed for other periods of aging and a different sample was used for each time. The top and bottom phases were analysed in a coupled GC-MS/FID (flame ionization detector) to determine their chemical compositions.

2.3 Chemical Composition of Top and Bottom Phases with Aging Time

2.3.1 Gas chromatography – mass spectrometry

The samples from top and bottom phases were analysed by gas chromatography-mass spectrometry (GC-MS) coupled with a flame ionization detector (FID). The mass spectrometer was used to identify the various compounds while the flame ionization detector was used to determine their concentrations. The GC-MS/FID is a Shimadzu GCMS-QP2010 plus, equipped with auto sampler/injector and a capillary column (RTX-1701) of 30m x 0.25 mm i.d. (film thickness: 0.25 µm, column flow: 0.75 mL/min, carrier gas: helium, maximum temperature: 280°C). Samples were mixed with a 1-dodecanol internal standard solution at a 1:1 ratio, diluted with methanol at a 1:22 ratio, and filtered using 0.2 µm pore size TEFLON filters. Then, 1 µL of sample was injected with a split ratio of 1:20 while the column was maintained at 45°C for 3 minutes before being heated to 220°C at a rate of 5°C/min, then the column was heated to 280°C at a rate of 30°C/min, and held for 3 min. The identification of the peaks in the chromatogram was based on the comparison with standard spectra and/or on the retention time of known standards injected. Quantification of each group of compounds was done by manual integration of single ion chromatograms.

2.4 Prevention of Phase Separation of Bio-oil through Solvent Addition

Butanol, ethanol, isopropanol or propanol was individually added in different concentrations to bio-oil samples and the sealed samples were kept at 80°C in a water bath. Every one-hour period, the samples were cooled down, centrifuged for 20 minutes at 5000 rpm and checked for phase separation. These steps were followed until the samples became phase separated. The time taken for phase separation to happen was recorded.

2.5 Chemical Composition of Bio-oil during Aging with Isopropanol as a Solvent

Isopropanol was identified as the most effective of the tested solvents in preventing phase separation (Figure 5) during long storage periods. The changes in chemical composition of the bio-oil with aging in the presence of isopropanol (at 10 and 20 wt% concentrations) were, therefore, investigated. Sealed samples of BTG bio-oil and 10 wt% isopropanol were kept at 80°C in a water bath for 17 days and samples were taken for GC-MS/FID analysis at 24 hours interval at the beginning and at 2-3 days intervals later on. Once phase separation had occurred, the top and bottom phases were separated by decanting and samples were taken for GC-MS/FID analysis. The GC-MS/FID analysis and peak area calculations were done according to the method that is described in section II-C above. During GC-MS analysis, 57 chemical components were identified, and they were categorized into phenolics, sugars, ketones, esters, acids, furans and aldehydes groups.

2.6 Higher Heating Value

HHV was measured with the bomb calorimeter for each aged sample and both top and bottom phases in case of phase separation.

In Figure 2 and Figure 6, the terms x_1 and x_i are defined as given in the Equations (1) and (2) below. There, x1 gives the initial standardized composition of the chemical component k and xi gives the normalized composition of component k at the time “i” (in hours in Figure 2 and in days in Figure 6) under the accelerated aging period.

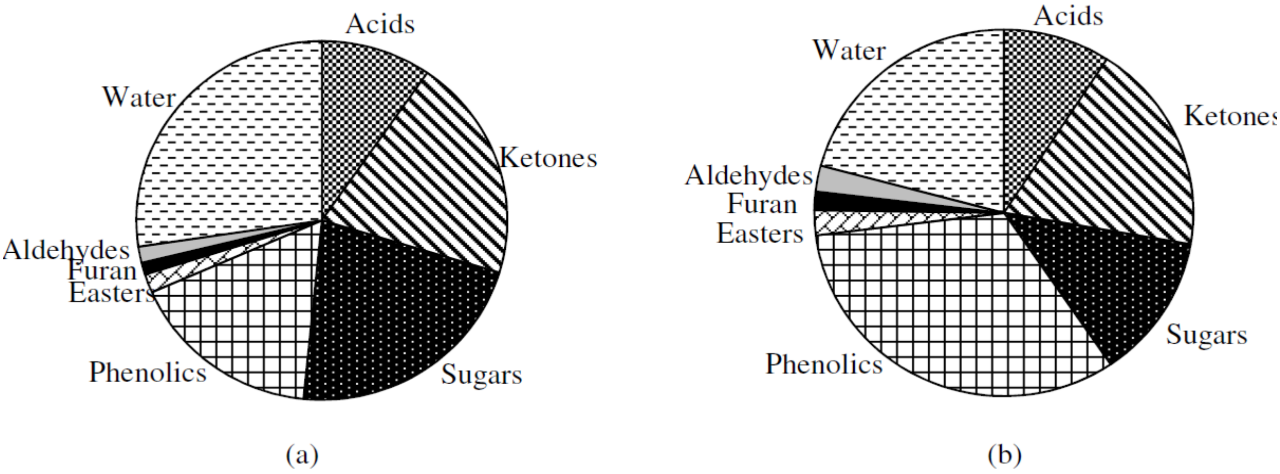


Fig. 1. The composition of top and bottom phases after phase separation occurs (at 24 hours). (a) top phase. (b) bottom phase.

$$x_1 = \frac{(\text{peak area of GC} - \text{FID for component k})\, at\ time\ 1}{(\text{peak area of internal standard})\, at\ time\ 1} \tag{1}$$

$$x_i = \frac{(\text{peak area of GC} - \text{FID for component k})\, at\ time\ i}{(\text{peak area of internal standard})\, at\ time\ i} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Is Phase Separation Effective?

Figure 1 shows the composition of top and bottom phases 6 hours after the initiation of phase separation. It is observed that the top phase contains a higher percentage of water and sugars and a lower share of phenolics when compared to the bottom phase. However, the concentrations of those components in both phases are still significant and the other components are also distributed in both phases. Therefore, the phase separation is not an effective method to segregate one or more of the component groups.

3.2 What Triggers Phase Separation?

Figure 2 shows the evolution of chemical composition of aged bio-oil during the accelerated aging process before phase separation occurs. The behaviour of a sample of BTG bio-oil during aging shows that, at first, some reactions occur relatively rapidly: for example, the results show that, after only 6 hours, the esters concentration has increased by about 50 %. After this initial period, the concentration of all the component groups that are observed in GC-MS/FID decreases with time. Since GC-MS can identify only the light compounds in the oil, this gives an indication that some of the components from each group might be disappearing from the light fraction through polymerization or condensation reactions.

3.3 What Happens after the Phase Separation Occurs?

Figure 2 shows the composition of bio-oil before phase separation.

Oasmaa *et al.* [38] show that the increase in water-insoluble compound is paired with the reduction in carbonyl compounds, such as esters, carboxylic acids, ketones and aldehydes, and this is correlated to the increase in molecular weight during aging. They show that the change in carbonyl compounds is due to reactions of aldehydes and ketones during storage, whose reaction products end up in the water-insoluble fraction. Similarly, Kim *et al.* [39] concluded that the decrease in concentration of most of the low molecular weight components in bio-oil during aging results from their chemical involvement in reactions with pyrolytic lignin. Their study also found that these reactions increase both the yield of pyrolytic lignin and the average molecular weight over the aging period [39].

Previous literature suggest that phase separation can be a result of the formation of water or heavy compounds as a by-product or as a result of polymerization and condensation reactions during aging [40]. However, in this study, as shown in Figure 3b, during aging of BTG bio-oil at 80°C, for the first three days the increase in the total water content is hardly noticeable. Boucher *et al.* [37] have also noticed that there was no significant increase or decrease of total water content during accelerated aging of bio-oil derived from softwood bark. Similarly, Kim *et al.* [39] found the same result during aging of poplar wood bio-oil at 23°C for a 10 weeks period. However, after phase separation, there is a significant difference of the water content between the top and bottom phases at any given time (Figure 3a). Even though the water content of the bottom phase slightly declined with time, this was due primarily to the increase of the weight of bottom phase through the migration of compounds other than water from the top phase to the bottom phase.

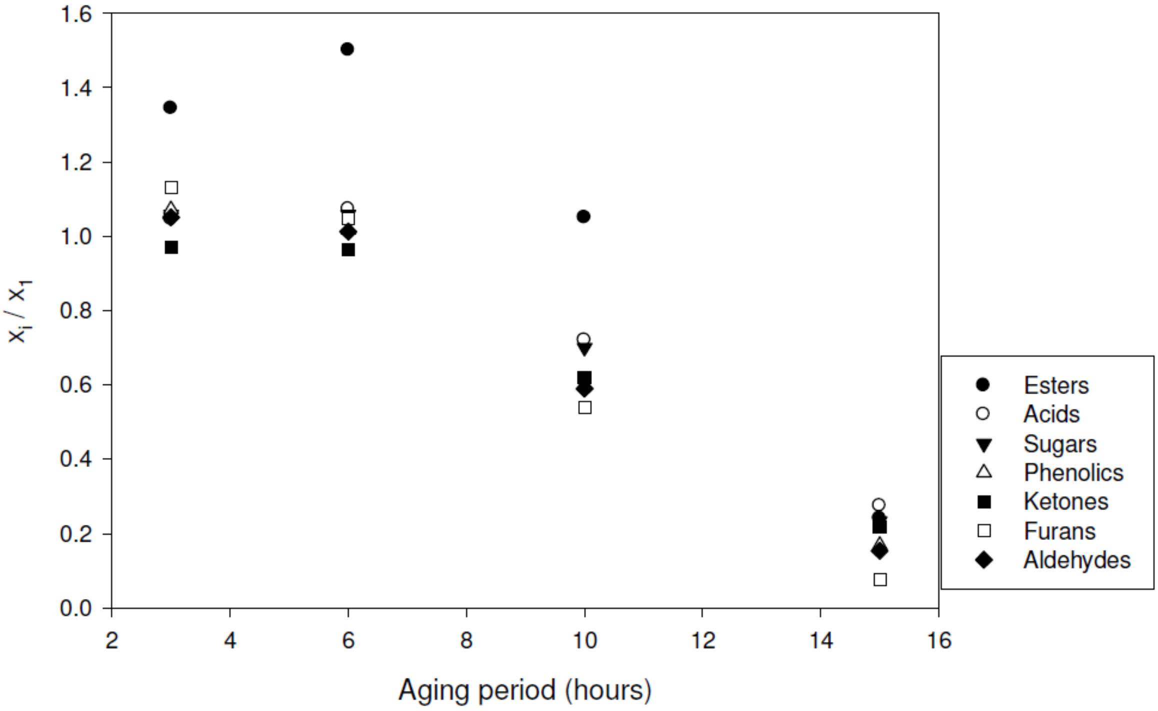
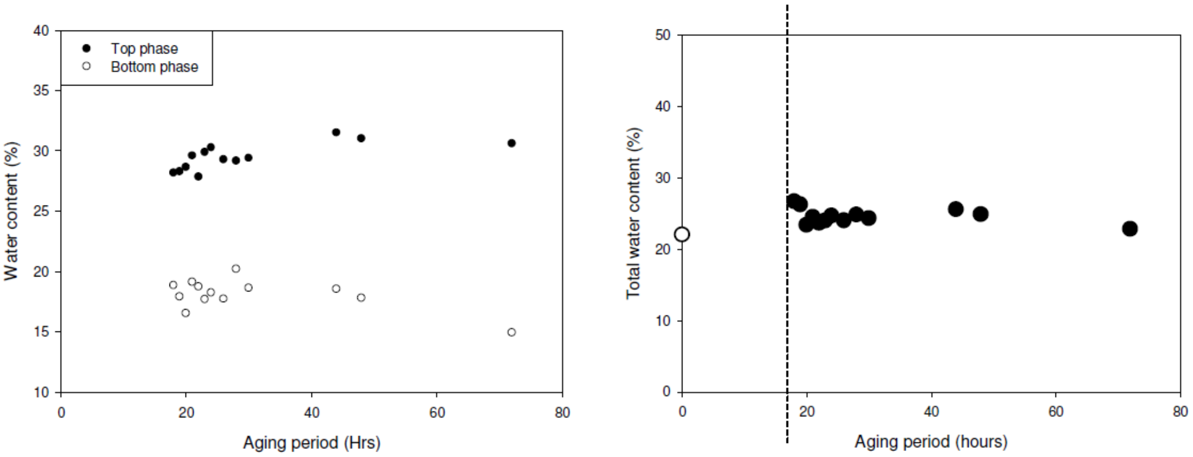


Fig. 2. Change in chemical composition of BTG bio-oil during aging at 80°C.



(a) (b)

Fig. 3. Water content of (a) Top and bottom phases of aged, centrifuged and settled bio-oil, and (b) the system (by water balance).

3.4 What Happens when Solvent are Added to Bio-oil?

Phase separation during storage can be prevented by adding the proper solvent. The impact of the addition of low concentrations (up to 10 wt%) of butanol, ethanol, isopropanol and propanol on the occurrence of phase separation is shown in Figure 4. Obviously the phase stability increases with increased proportion of additives. Isopropanol is the most effective of the four tested additives, since it keeps the oil in a single phase for the longest duration at 80°C. 10 % addition of isopropanol prevents the phase separation for 13 days at 80°C. In the same way, Boucher *et al.* [37] showed that 15 % addition of methanol will increase the phase stability of bio-oil.

There are two possible explanations for the inhibition of phase separation observed with the addition of low molecular weight alcohol: the alcohol could increase the mutual solubility of the polar and non-polar bio-oil components or, alternately, alcohols may react with some of the bio-oil components. The change in chemical composition of bio-oil treated with 10 wt% of isopropanol is shown in Figure 5. Prior to phase separation, the major changes are the decline in phenolics, ketones and aldehydes and the increase of esters. Similar results have been observed in a several previous studies [2], [3], [38], [41]. The acid content is slightly decreased. After 13 days of aging at 80°C, the aqueous phase, which is rich in sugars, and the organic phase, which is rich in phenolics, separated. The decrease in phenolics, ketones and aldehydes might have changed the mutual solubility of the bio-oil components, or the formation of high molecular weight components through polymerization or condensation reactions might have reduced their mutual solubility. Diebold [1] also argues that as the bio-oil composition changes during aging, the mutual solubility of the components changes to make phase separation more likely. Diebold also argues that the increasing difference in polarity among the compounds in the aged bio-oil increases the tendency for phase separation [1]. For example, esterification converts highly polar organic acid and alcohol molecules into esters with relatively low polarity and extremely polar water. The formation of acetals shifts the composition away from acetaldehyde hydrates, releasing the water of hydration and the water formed with the acetal. Acetals are in the relatively nonpolar family of ethers.

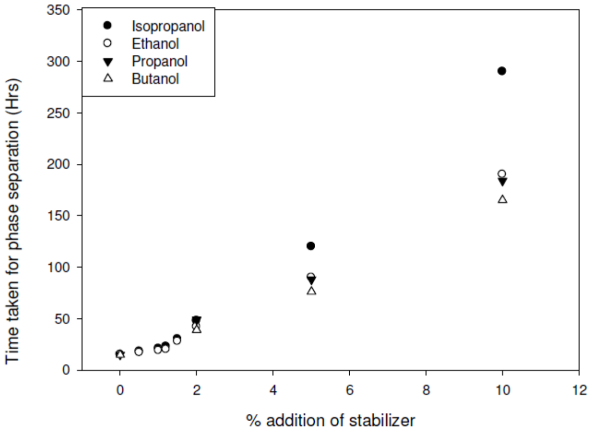


Fig. 4. Time taken for phase separation to occur at different percentage of stabilizers, under accelerating aging conditions (at 80°C).

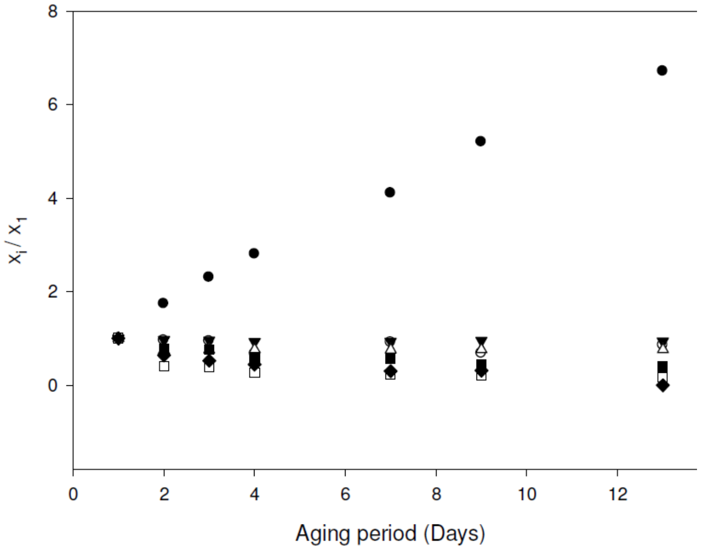


Fig. 5. Change in chemical composition of BTG bio-oil with 10 % isopropanol during aging at 80°C.

The study by Hu *et al.* [12] shows that phenolic compounds (phenol, guaiacol and vanillin *etc*.) are reactive in an acidic environment. This is confirmed by the decrease in total phenolic compounds observed in this study. Qu *et al.* [42] concluded that the majority of carbohydrates and sugars in the bio-oil come from the cellulose fraction of biomass, while the majority of phenolics come from the lignin fraction. They also found out that the hemicellulose is the fraction which mainly contributes towards the acid, ketone and aldehydes contents of the bio-oil [42].

When the isopropanol concentration is increased from 10 % to 20 %, the proportion of esters continues to increase and acids to decrease. There is no measurable impact on ketones, furans and aldehydes. It can be concluded from these results that the addition of polar solvents (isopropanol in this case) not only changes the mutual solubility of components but also changes the chemical composition through reactions such as the esterification of carboxylic acids.

3.5 Change in the Higher Heating Value (HHV) of Bio-oil with Isopropanol Added as a Solvent

Figure 6 shows the evolution of the higher heating value (HHV) of bio-oil with the addition of 10 % or 20 % isopropanol, as well as the combined values of top and bottom phases based on their weight percentages during aging at 80°C after the phase separation. The addition of isopropanol prevents the deterioration of HHV of bio-oil that happens during aging.

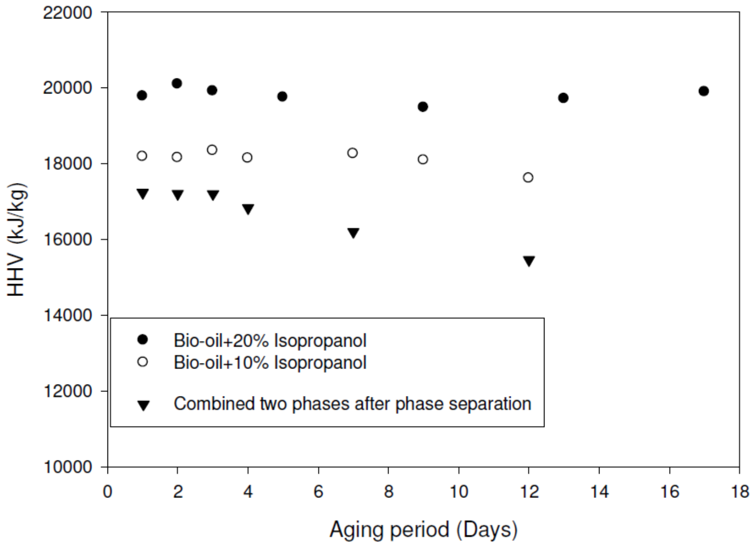


Fig. 6. Change in HHV of bio-oil with 10 % and 20 % isopropanol and combined top and bottom phases without solvent (values are combined based on their weight % at respective time of aging).

4. CONCLUSIONS

Natural phase separation of bio-oil is not an effective tool to segregate undesired components into a single phases. It does not effectively remove the acids or water or other detrimental components groups into a single phase.

During aging of bio-oil at 80°C, phase separation of hardwood derived bio-oil occurs after about 15 hours. During GC-MS analysis, 57 chemical components were identified and they were categorized into phenolics, sugars, ketones, esters, acids, furans and aldehydes groups. GC-MS analysis shows that some of these components disappear from the bio-oil during accelerated aging. These components may undergo polymerization or condensation with the heavier bio-oil components resulting in increased average molecular weight.

The addition of solvents greatly retards phase separation and increase the storage life while keeping the oil as a single phase. Amongst the tested alcohols in this study, Isopropanol is the most suitable alcohol to retard phase separation. The addition of a polar solvent, such as isopropanol, not only increases the mutual solubility of the components in bio-oil, but also modifies the chemical composition of the bio-oil through reactions such as esterification. By adding 10% isopropanol, the shelf life can be increased to 13 days at 80 ºC.

ACKNOWLEDGEMENT

The author would like to thank Prof. Franco Berruti and Prof. Cedric Brians at The Institute of Chemicals and Fuels from Alternative Resources (ICFAR), Western University, London, Ontario, Canada for their valuable guidance and supervision during the research project. Appreciations are also extended for Natural Sciences and Engineering Research Council of Canada for the financial support through the Western University, London, ON Canada.

REFERENCES

[1] Diebold J.P., 2000. *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils.* NREL/SR-570-27613. National Renewable Energy Laboratory, Colorado.

[2] Diebold, J.P. and S. Czernik. 1997. Additives to lower and stabilize the viscosity of pyrolysis oil during storage. *Energy & Fuels 1997* 11: 1081-1091.

[3] Oasmaa A. and E.Kuoppala. 2003. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy & Fuels 2003* 17: 1075-1084.

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

[5] Oasmaa A. and S. Czernik. 1999. Fuel oil quality of biomass pyrolysis oils- state of the art for the end users. *Energy & Fuels 1999* 13: 914-921.

[6] Demirbas A., 2007. The influence of temperature on the yield of compounds existing in bio-oils obtained from biomass samples via pyrolysis. *Fuel Processing Technology* 88(2007): 591-597.

[7] Batts B.D. and A.Z. Fathoni. 1991. A literature review on fuel stability with particular emphasis on diesel oil. *Energy & Fuels 1991* 5: 2-21.

[8] Vispute T., 2011. *Pyrolysis oils: Characterization, stability analysis and catalytic upgrading to fuels and chemicals*. Open access dissertation, paper 349, University of Massachusetts, Amherst. Retrieved from the World Wide Web: http://scholarworks.umass.edu/open_access_dissertations/349

[9] Kim T.S., Kim J.Y., Kim K.H., Lee S. and Choi D., 2012. The effect of storage duration on bio-oil properties. *Journal of Analytical and Applied Pyrolysis* 95(2012): 118-125.

[10] Oasmaa A., Elliott D.C., and Korhonen J., 2010. Acidity of biomass fast pyrolysis bio-oil. *Energy & Fuels 2010* 24: 6548-6554.

[11] Hu X., Gunawan R., Mourant D., Lievens C., Li X., Zhang S., and Chaiwat W., 2012. Acid-catalysed reaction between methanol and bio-oil from fast pyrolysis of mallee bark. *Fuel* 97(2012): 512-522.

[12] Hu X., Mourant D., Wang Y., Wu L., Chaiwat W. Gunawan R., Gholizadeh M., Lievens C., Garcia-Perez M., and Li C. Z. (2013). Acid-catalysed treatment of the mallee eaf bio-oil with methanol: Effects of molecular structure of carboxylic acids and esters on their conversion. *Fuel Processing Technology* 106(2013): 569-576.

[13] Wang J.J., Chang J., and Fan J., 2010. Upgrading of bio-oil by catalytic easterification and determination of acid number for evaluating esterification degree. *Energy & Fuels 2010* 24: 3251-3255.

[14] Moens L., Black S.K., Myers M.D., and Czernik, S., 2009. Study of the neutralization and stabilization of a mixed hardwood bio-oil. *Energy & Fuels 2009* 23: 2695-2699.

[15] Li. X., Gunawan R., Lievens C., Wang Y., Mourant D., Wang S., Wu H., Garcia-Perez M., and Li C.Z., 2011. Simultaneous catalytic esterification of carboxylic acids and acetalisation of aldehydes in fast pyrolysis bio-oil from mallee biomass. *Fuel* 90(2011): 2530-2537.

[16] Zhang Q., Chang J., Wang T., and Xu Y., 2006. Upgrading bio-oil over different solid catalysts. *Energy & Fuels 2006* 20: 2717-2720.

[17] Song M., Zhong Z., and Dai J., 2010. Different solid acid catalysts influence on properties and chemical composition change of upgrading bio-oil. *Journal of Analytical and Applied Pyrolysis* 89(2010): 166-170.

[18] Boucher M.E., Chaala A., and Roy C., 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbine. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass and Bioenergy* 19(2000): 337-350.

[19] Ikura M., Stanciulescu M., and Hogan E., 2003. Emulsification of pyrolysis derived bio-oil in diesel fuel. *Biomass and Bioenergy* 24(2003): 221-232.

[20] Weerachanchai P., Tangsathitkulchai C., and Tangsathitkulchai M., 2009. Phase behaviors and fuel properties of bio-oil-diesel-alcohol blends. *World Academy of Science, Engineering and Technology* 56(2009): 387-393.

[21] Jiang X. and N. Ellis. 2010. Upgrading bio-oil through emulsification with biodiesel: Thermal stability. *Energy & Fuels 2010* 24: 2699-2706.

[22] Yin Q, Wang S., Li X., Guo Z., and Gu, Y., 2010. Review of bio-oil upgrading technologies and experimental study on emulsification of bio-oil and diesel. In *International Conference of Optoelectronics and Image Processing 2010*, 343-347.

[23] Udomsap P., Yeinn Y.H., Hui J.T.H., and Yoosuk B., 2011. Towards stabilization of bio-oil by addition of antioxidants and solvents and emulsification with conventional hydrocarbon fuels. In *International Conference and Utility Exhibition*, Thailand, September 2011. Retrieved from the World Wide Web: http://www.serd.ait.ac.th/icue2011/cd/papers/S11/S%2011.3.pdf

[24] Venderbosch R.H., Ardiyanti A.R., Wildschut J., Oasmaa A., and Heeres H.J., 2009. Stabilization of biomass derived pyrolysis oils. *Journal of Chemical Technology and Biotechnology 2010* 85: 674-686.

[25] Qiang L., Xu-lai Y., and Xi-feng Z., 2008. Analysis on chemical and physical properties of bio-oil pyrolysis from rice husk. *Journal of Analytical and Applied Pyrolysis* 82(2008): 191-198.

[26] Boucher M.E., Chaala A., Pakdel H., and Roy C., 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbine. Part II: Stability and aging of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass and Bioenergy* 19(2000): 351-361.

[27] Oasmaa A., Sipila K., Solantausta Y., and Kuoppala E., 2005. Quality improvement of pyrolysis liquid: Effect of light volatiles on the stability of pyrolysis liquids. *Energy & Fuels 2005* 19: 2556-2561.

[28] Zuo-gang G., Shu-rong W., Ying-ying Z., Zhong-yang L., and Ke-fa C., 2009. Separation of acid compounds for refining biomass pyrolysis oil. *Journal of Fuel Chemistry and Technology* 37(1): 49-52.

[29] Siriwardhana M., 2020. Fractional condensation of pyrolysis vapours as a promising approach to control bio-oil aging: Dry birch bark bio-oil. *Renewable Energy 152* (2020): 1121-1128.

[30] Siriwardhana A.G.M.T., 2013. Aging and stabilization of pyrolytic bio-oils and model compounds. *Electronic Thesis and Dissertation Repository*. 1719, Western University, London, Ontario, Canada. Retrieved from the World Wide Web: http://ir.lib.uwo.ca/etd/1719, 2013.

[31] Chen H.W., Song Q.H., Liao B., and Guo Q. X., 2011. Further separation, characterization and upgrading for upper and bottom layer from phase separation of biomass pyrolysis oils. *Energy & Fuels 2011* 25: 4655-4661.

[32] Ba T., Chaala A., Garcia-Perez M., Rodrigue D., and Roy C. 2004. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Characterization of water-soluble and water-insoluble fractions. *Energy & Fuels 2004* 18: 704-712.

[33] Song Q.H., Nie J.Q., Ren M.G., and Guo Q.X., 2009. Effective phase separation of biomass pyrolysis oils by adding aqueous salt solutions. *Energy & Fuels 2009* 23: 3307-3312.

[34] Scholze B., Hanser C., and Meier D., 2001. Characterization of water- insoluble fraction from fast pyrolysis liquids (pyrolysis lignin). Part II: GPC, carbonyl group and C-NMR. *Journal of Analytical and Applied Pyrolysis* 58-59(2001): 387-400.

[35] Scholze B. and D. Meier. 2001. Characterization of water- insoluble fraction from fast pyrolysis liquids (pyrolysis lignin). Part I: PY-GC/MS, FTIR and functional groups. *Journal of Analytical and Applied Pyrolysis* 60(2001): 41-54.

[36] Xu J., Jiang J., Lv W., Dai W., and Sun Y., 2010. Rice husk bio-oil upgrading by means of phase separation and production of esters from the water phase and novolacresins from the insoluble phase. *Biomass and Bioenergy* 34(2010): 1059-1063.

[37] Boucher M.E., Chaala A., Pakdel H., and Roy C., 2000. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbine. Part II: Stability and aging of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass and Bioenergy* 19(2000): 351-361.

[38] Oasmaa A., Korhonen J., and Kuoppala E., 2011. An approach for stability measurement of wood-based fast pyrolysis bio-oil. *Energy & Fuels 2011* 25: 3307-3313.

[39] Kim T.S., Kim J.Y., Kim K.H., Lee S., and Choi D., 2012. The effect of storage duration on bio-oil properties. *Journal of Analytical and Applied Pyrolysis* 95(2012): 118-125.

[40] Naske C.D., Polk P., Wynne Z., Speed J., Holmes W.E., and Walters K.B., 2012. Postcondensation filtration of pine and cottonwood pyrolysis oil and impacts on accelerated aging reaction. *Energy & Fuels 2012* 26: 1284-1297.

[41] Lievens C., Mourant D., He M., Gunawan R., Li X., and Li C. Z., 2011. An FT-IR spectroscopic study of carbonyl functionalities in bio-oils. *Fuel* 90(2011): 3417-3423.

[42] Qu T., Guo W., Shen L., Xiao J. and Zhao K., 2011. Experimental study of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. *Industrial and Engineering Chemistry Research* 50(2011): 10424-10433.