Abstract—Bio-oil has been recognized as a promising renewable energy resource and important feedstock for valuable chemicals. Unfortunately, bio-oil needs upgrading before it can be used as fuel or sources of downstream chemicals. This is due to the complex properties of the bio oil and variable compositions encountered over time. The fractionation of bio oil by traditional distillation quit often leads to form a solid residue of coke and gums consequently formed from polymerization of the mixture components. The use of microbubble distillation is a novel approach used for the distillation of bio oils to avoid the decomposition characteristics observed using traditional methods. In this study a mixture of water, acetic acid, cyclohexanone and salicylaldehyde was chosen as the representative of bio-oil components. The separation extent of water and acetic acid from mixture was observed during the experiment, while varying liquid level and sparge air temperature, showing the effect on the performance of microbubble distillation. The results showed the minimal liquid temperature rise was achieved during the experiment, consequently, no solid residue or polarization between the components was observed in all experiments. In addition, by reducing of the liquid level the evaporation rate increase for both water and acetic acid. At a liquid level of 2mm, the mixture was free of water after 60 min and 70% of acetic acid was removed. Increasing the air temperature by 30°C, 86% of acetic acid was removed.

Keywords—Microbubble distillation, bio oil, bio oil model component

1. Introduction

In recent decades, the demand of fossil fuels has been observed to grow globally, due in part to an ever increasing population. However, concern has been raised about the non-renewability of fossil fuels, source limitations, and contributed in CO₂ emissions. Recently, bio oils have received attention and interest as potential substitutes for traditional petroleum-derived fuels and of wide range of valuable chemicals [1, 2].

Nonetheless, the undesirable properties of bio oil including water content, high acidity, high viscosity, high oxygen content, lower heating value and relatively instability limit the direct utilization of bio oil as fuel or chemicals [3].

The low acidity of the oil cause corrosion in equipments and promoted several polarization and condensation reactions[3-5].

The present of water reduce the viscosity of bio oil thus enhance the flow properties of bio oil, but reduces the heating value and flame temperature concurrently. Also, this increases the delay in ignition and reduces the combustion rate [6-8].

The presence of functional groups within the composition of bio oil components, e.g. phenols, carboxylic acids, ketones and aldehydes, can cause significant changes in bio-oil properties with time and temperature. Polymerization, condensation and other aging reactions take place during storage or when the bio-oil is heated. Several chemical and physical upgrading method have been proposed to optimize the quality bio-oil, such as esterification[9,10], hydroprocessing[11], catalytic cracking[12], liquid chromatography[13], emulsification [14] and molecular distillation[15].

Thermal sensitivity of bio oil makes separation processing by traditional distillation problematic. The distillation process involves high temperatures and long resident times, that lead to several polymerization reactions, gum and char formation, and modification in bio oil properties. Even in vacuum distillation, a process aiming to remove the water and lighter fractions from bio oil, it was reported that when the liquid temperature rose to 100 °C or more, rapid polymerization and other aging reactions were occur, resulting in char formation and a solid residue which approximately 50% of the biomass[1, 3].

The basic fundamentals of Microbubble distillation have been established by Zimmerman[16]. A computation model has been developed to investigate the concept of non-equilibrium evaporation by heating the gas phase rather than the liquid phase. In traditional distillation the liquid is boiled to achieve the maximum equilibrium vapour pressure. The computation model hypothesis takes into consideration the internal gas dynamics of the bubble. The model also explores the impact of microbubbles on the mechanisms of sensible heat transfer and evaporation. The model shows that by controlling the bubble residence time in the liquid phase, maximum evaporation can be achieved. For a hot air bubble rising in water, the maximum absolute humidity is obtained after short time from bubble detachment. Thereafter, if the bubble is still hot enough, the contact between the bubble and

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the liquid phase promotes sensible heat transfer from the bubble to the liquid. The sensible heat transfer cause cooling of the bubble accompanied by condensation of vapour back into the liquid phase. Thereafter, a binary mixture of ethanol and water was distillate by micobubble distillation. A high separation efficiency was achieved and the vapour–liquid composition was higher than that obtained under equilibrium conditions[17].

The present study aims to investigate the upgrading of bio oil by microbubble distillation. A bio-oil model component contains water, acetic acid, cyclohexanone and salicylaldehyde was used in the study. The concentration of the water and acetic acid was monitored during the experiments to show the effect of the liquid level and air temperature on the performance of microbubble distillation. Microbubble distillation has never been applied in upgrading the bio oil before.

II. Experimental Work

The microbubble distillation experiments were performed using batch system as shown in fig.1. The experiments are conducted with fluidic oscillator to generate a microbubble cloud [18, 19]. The separation tank is made of glass fixed on stainless steel base. The micro-porous diffuser is 60*120*5mm with pore diameter of 20μm, manufactured from ceramic materials (Point Four Systems Inc.). The air stream was heated and fed to the fluidic oscillator then to the tank through a micropore diffuser. Consequently, the desired flow rate of the air inter the tank is controlled by the bleed valves. The flow rate is measured from the tank outlet which was kept constant at 3liter/min.

The initial volume of the liquid in the tank was prepared according to the required liquid level above the diffuser. The approximate volume was calculated as following:

\[ V(\text{required}) = \text{Area of separation tank base} \times H \]  
\[ (H) \text{ is the liquid level}. \]  

The air was supply to the heater at flow rate of 80 litre/min. The liquid mixture was poured into the tank, after the desired air temperature was reached.

The mixture components composition was kept constant for all experiments at 15% water, 15% acetic acid, 33% cyclohexanone and 32% salicylaldehyde.

Samples of the liquid were taken every 30 min along the experimental duration. The temperature reading was taken every ten minutes.

The quantitative and qualitative analyses of mixture were performed by a GCMS-QP2010SE (SHIMADZU). DB-1MS capillary column(59.4m,0.25um,0.25mm) was equipped to the GC-MS. Helium was used as the carrier gas. 0.3 ml of sample was injected at 250°C with a split ratio of 500. The identification of component was done by matching the mass spectrum with spectral library. Set of standard solutions was used to make the calibration curve to cover the concentration rage of the component.

III. Result and discussion

A. The effect of the liquid level

Two liquid levels of 3.5 and 2 mm were used to study the effect of the liquid level on the separation of water and acetic acid from the mixture. The temperature of the injected air was fixed at 70°C.

Fig.2 shows the redaction in water concentration with time. The water concentration drops to 1.2% after 60 min at liquid level of 2mm. The mixture become free of water during the experimental time between 60 to 90 min. The increasing in the liquid level reduces the water separation effectively, where the concentration of water reduced from 15% to 5% in 60 min at liquid level of 3.5 mm.

The redaction in acetic acid concentration with time at liquid level of 3.5 and 2mm is shown in fig.3. The concentration of the acetic acid increased within the first period of operation for both liquid levels, thereafter, the concentration decreases until it reach 4.3% after 120 min at liquid level of 2mm. While the final concentration of the acetic acid was 11.7% at liquid level of 3.5mm.

The evaporation rate of components from liquid phase to the vapour phase is related to the components volatility. The volatility of water is higher than that that of acetic acid and the rest of the mixture component. Thus evaporation rate of water is the highest. The water molecule transfer from the liquid phase surrounding the bubble interface to the vapour phase, result in sharp reduction of water concentration and increasing the acetic acid concentration which evaporate slowly. Subsequently, the liquid at the bubble interface become enriched in acetic acid molecules and the water molecules become less due to the low water concentration in the bulk. Consequently, the amount the acetic acid transfer to the vapour increase and bulk concentration of acetic acid decreases.

The liquid mixture temperature increases by approximately 5 °C during the experiment time at liquid level of 3.5 mm. The liquid temperature increases by 7°C at lower liquid level of 2mm as shown in fig.4. However, most of the bubble enthalpy
is consumed as latent heat of evaporation, and the heat transfer to the liquid is combination of the heat transfer from the bubble to the liquid, and the heat transfer from the diffuser.

The mass spectra obtained from the GC-MS for the samples after 90min and 120min for mixture at liquid level of 3.5 mm and 2mm presented in fig.5 and 6. The peaks detected in the samples were for water at retention time of 3.45min, acetic acid peak at retention time of 4.17 min, cyclohexanone peak at retention time of 7.83 min, finally peak at retention time of 11.27 min for the salicylaldehyde. The spectra show no evidence of any of polymerization and condensation reactions between the mixture components were developed.

**Figure 2** the water concentration profile at liquid level of 3.5mm and 2mm.

**Figure 3** The acetic acid concentration profile at liquid level of 3.5mm and 2mm.

**Figure 4** Liquid temperature profile at liquid level of 3.5mm and 2 mm.
B. The effect of air temperature

Additional experiments were carried out to explore the effect of the air temperature on the performance of microbubble distillation. The temperature of the air was raised to 100°C at liquid level of 2mm. The water content in the mixture drops more sharply by increasing the temperature of the air stream as presented in fig.7. The total water removed after 60 min which was much greater in comparison with air temperature of 70°C. Increasing the air temperature also improve the acetic acid stripping from the mixture. Fig.8 shows a compression between the acetic acid concentration profile at air temperature of 100°C and 70°C. After 120 min of the experiment time at air temperature of 100°C, 86% of the acetic acid was removed from the mixture, while 70% of the acetic acid was removed at the end of the experimental time when the air temperature was 70°C. However, the trend of the concentration profile is still similar in both air temperature.

The partial pressure of a component is a function of temperature. Raising the air temperature leads to an increase of the partial pressure of the component. Consequently, the volatility of the component and the evaporation rate will increase.

The temperature of the liquid mixture increased by 10.5°C at air temperature of 100°C as shown in fig.9.

Although the increase of air temperature results in increasing of the liquid mixture, the separation rate of water and acidic acid were increased. Moreover, the GC-MC spectra shows no polymerization or other reaction has been developed due to the increase of air temperature for all samples during experimental time. Fig.10 shows the GC-MS spectra of the liquid samples at 90 min and 120 min at air temperature of 100°C. This clearly Indicates that no additional peaks are detected in the samples except that of water, acetic acid, cyclohexanone and salicylaldehyde.

The removal of water and acetic acid from the pyrolysis oil contributes to increasing its heating value, reducing the corrosivity and increases the stability of the bio oil. Moreover, the removal of water is essential for catalytic upgrading of bio oil, where the water found to have negative effect on the catalyst[20].

IV. Conclusion

In the current study, Microbubble distillation has been employed to separate water and acetic acid from bio oil model mixture. The bio oil model component used in the study contained water, acetic acid, cyclohexanone and salicylaldehyde. The effect of liquid level and air temperature on the performance of the microbubble distillation was investigated. The results show that microbubble distillation can achieve high separation with minimal rise in liquid temperature. Thus, separation of the component from the mixture can be achieved without polymerization or coking of the mixture component. The evaporation rate enhance by decrease the liquid level. Furthermore, increase in air temperature significantly affects the evaporation rate of the water and acetic acid. Microbubble distillation is a promising technology to separate the thermal sensitive mixtures like bio oil. The batch system used in the study is first attempt to prove the concept and study the performance of the microbubble distillation and the effect of the operation parameters. More study is currently on going to improve the separator design and developing the system operation for continuous fractional distillation.
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