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Effect of Dry Steam on Nature and Quality of Selected Characteristic Organic Chemicals

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Abstract. In this study, effects of steam with different density (saturated and dry steam) on five characteristic organic chemicals such as alcohol, ester, aromatics, phenol and fatty acid were investigated below 200 °C. The natures of the tested organic chemicals were analyzed by weight loss in steam. The experimental results showed that the dissolving behavior of each organic compound in steam is significantly different. Alcohols and phenanthrene can dissolve easily in steam with low density; High saturated fatty acid cannot almost dissolve in steam below 200 °C; Ester are less stable in saturated steam; Phenols revealed a variable behavior characterized by an increase of weight at early stage and a decrease later in saturated steam, and companied by color change. It must be necessary to consider proper steam density condition for selective extraction of some special chemicals.

Keywords: Effect, Dry steam, Characteristic organic chemical
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INTRODUCTION

Because of environmental and economic reasons, superheated and sub-critical processes are nowadays becoming appealing for industrial applications. It has been shown, for example, that by using nearcritical-superheated steam, it is possible to synthesize silicate film onto the surface of SUS pipe [1]; by using subcritical-water technology, it is possible to extract polycyclic aromatic hydrocarbon from soil [2,3]. Whichever mentioned above, it was believed that the enhancement of solubility of materials or the acceleration of reaction, are driven primarily by the augmentation in the fluid density. However, it was not always interesting for some special reactions, such as extraction of natural compounds from biomass. Reversely, it was argued that eliminating pressure out of reaction ambience (for example, certain vacuum technique) was useful for improving the yields of some natural compounds such as steroid, ester, alkene and aromatics [4,5]. On the other hand, improving temperature was another necessary factor to be considered. Therefore, superheated steam, with high temperature but relatively low pressure, becomes an expectable reaction medium for extraction of some natural organic compounds. Recent reports showed that superheated steam is an effective method for increasing yield of pyrolysis oil from biomass and production of some special biomass-derived chemicals [6-9]. However, if summing up these pyrolysis products obtained at different temperature range, it was always difficult to do such affirmation regarding these products being the direct extractives or decomposition products of native compounds because of the complication of biomass constitution and the thermolabile nature for most organic materials. Much previously reported work focused on studying the total yield of different compounds, a little work has been done about the solubility of mono-component itself in reaction medium. Therefore, it was necessary to do some basic determination about the solubility of characteristic organic compound in steam. These processes are the basic steps for industrial application such as steam-distillation extraction and new formulations of pharmaceuticals.

In this work, effect of steam with different density (saturated and dry steam) on the nature of the selected characteristic organic chemicals was investigated through determining their solubility in steam. A batch-type reactor was used and a wholly weight loss of samples in a closed system was determined to evaluate the solubility of samples. Especially dry steam, which was defined to be a superheated steam below 200 °C with lower density of steam, was cared for its extraction properties.

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EXPERIMENTAL

Five kinds of characteristic organic compounds: palmitic acid ($CH_3(CH_2)_{14}COOH$), methyl palmitate ($CH_3(CH_2)_{14}COOCH_3$), phenanthrene ($C_{14}H_{10}$), hydroquinone ($C_6H_4(OH)_2$), myristyl alcohol ($CH_3(CH_2)_{13}OH$), were from Wako Pure Chemical Industries Ltd.(Osaka). Their properties were listed in Table 1.

A schematic diagram of the reactor is shown in Fig.1, which was an autoclave packed an inner Teflon reactor with a volume of 80 ml. A simple method is proposed to valuate the dissolving behavior of steam for organic materials by determining the solubility of selected compounds. The solubility here was defined to be the amount (mg) dissolved in unit volume steam (liter), which was calculated from the total weight loss of starting materials after reaction.

During reaction, sample was packaged in a glass vessel that was put on a stainless steel mesh (SUS316) braced with a Teflon pipe. Before reaction, sample and glass vessel was weighed [W_0], after reaction, the residual sample and grass vessel was dried and weighed [W (mg)] again. Solubility of sample, X [mg/l], was expressed by the weight loss of sample, as

$$X = 1000 \times \frac{W_0 - W}{80} \qquad (1)$$

According to fundamental principles of physics, generation of steam was achieved by adding proper amount of water into Teflon reactor as well as heating. The amount of water added is calculated according to gas equation formula, as

$$PV=nRT \qquad (2)$$

Temperature is controlled by a heating oven; R-gas constant, V-volume of Teflon reactor (80 ml); P-reaction pressure, n-mol of water added into the reactor.

TABLE 1. Properties of selected characteristic organic compounds.

Assortment	Compound	Chemical Formula	Molucular Weight	Purity (%)	Boiling point (^oC)
Fatty acid	Palmitin acid	$CH_3(CH_2)_{14}COOH$	256.43	95	360
Ester	Methyl palmitate	$CH_3(CH_2)_{14}COOCH_3$	270.46	95	190.5
Alcohol	Myristyl alcohol	$CH_3(CH_2)_{13}OH$	214.39	99	170 (20 mmHg)
Aromatic	Phenanthrene	$C_{14}H_{10}$	178.23	95	340
Phenol	Hydroquinone	$C_6H_4(OH)_2$	110.11	99	285

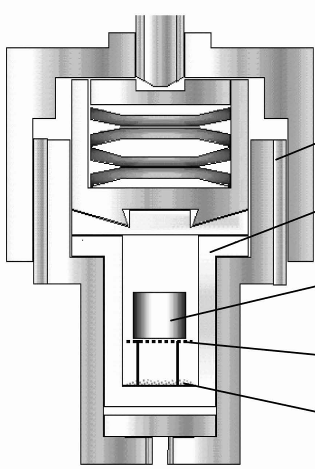

FIGURE 1. Schematic illustration of the batch-type reactor.

RESULT AND DISCUSSION

As shown in Fig. 2, solubility of each organic compound in steam was considerably different. Alcohols and phenanthrene can dissolve easily in steam with less density (Fig. 2 (a) and (b)) despite reaction temperature (140 ˚C) was far lower than their boiling point. As high temperature and less amount of water resulted in a lower steam density in reactor, this caused alcohol to evaporate more quickly, whilst high sublimation property of aromatics was responsible for the larger weight loss of phenanthrene in hot air, which can be supported by the phenomenon that when cooled to room temperature after reaction, sample was seen to recrystallize onto the wall of reactor. On the other hand, whichever myristyl alcohol or phenanthrene, when opening the reactor after reaction, it was seen that cooling drops of steam and sample assemblage (white crystalloid) kept separate. Therefore, it

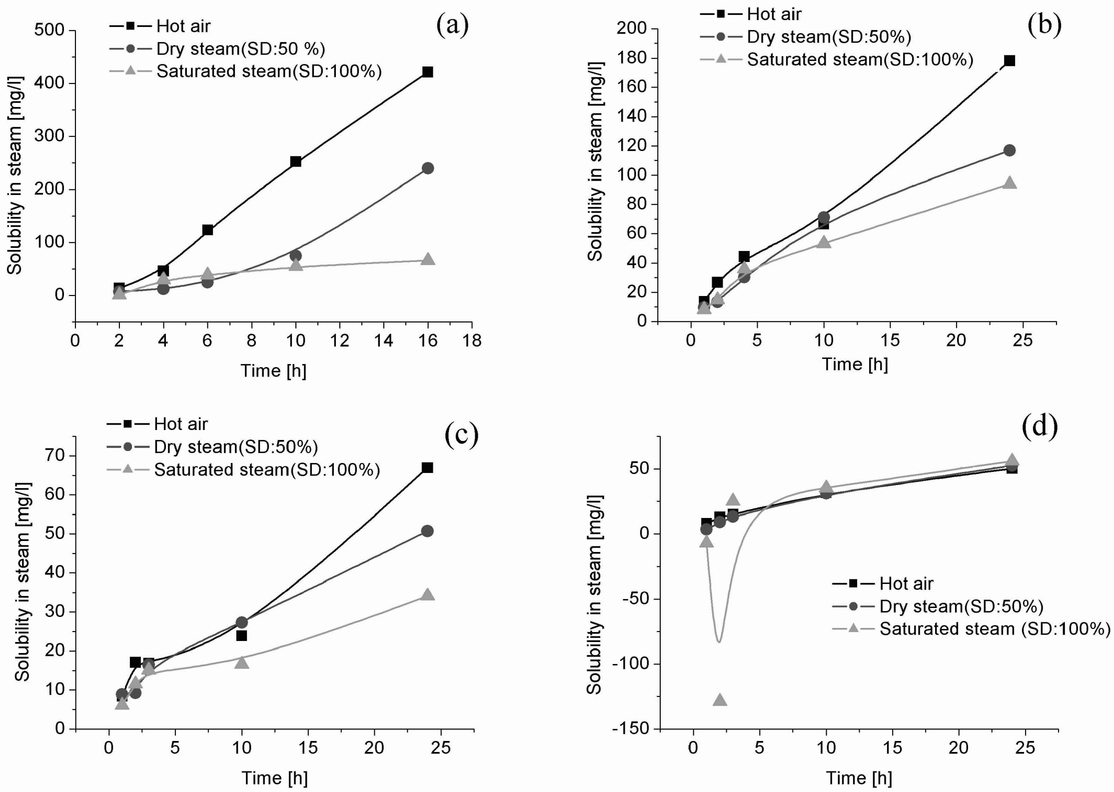

FIGURE 2. Solubility curves of four characteristic organic compounds in steam at 140 ˚C. (a) Myristyl alcohol (b) Phenanthrene (c) Methyl palmitate (d) Hydroquinone.

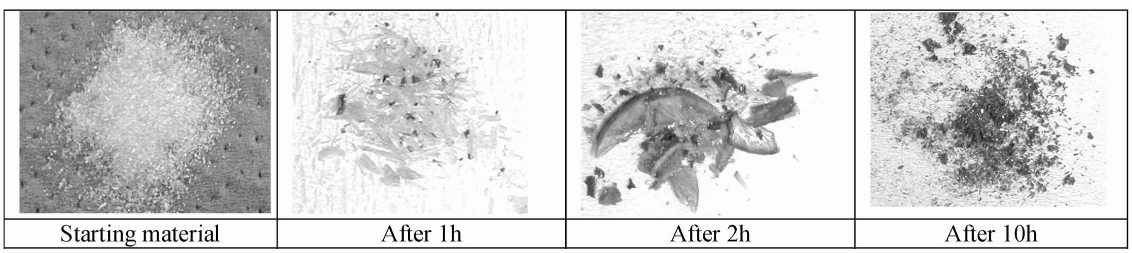

FIGURE 3. Color change of hydroquinone in saturated steam at 140 ˚C.

suggested that it is more exact to say alcohol evaporating in steam not dissolving in steam. Solubility here just indicated difficult or ease for evaporation of tested compounds, and didn't show the exact meaning for dissolving itself.

As shown in Fig. 2 (c) and (d), ester and phenol showed lower solubility in steam. Hydroquinone has revealed a variable behavior characterized by an increase of weight when exposed into saturated steam 2 h and a decrease later (Fig. 2 (d)), and furthermore, companied with a color change from white to dark brown as shown in Fig. 3. At the same time weight change showed that density of steam has no significant effect on dissolving hydroquinone.

Similarly, methyl palmitate showed a low but a little high solubility than that of hydroquinone (Fig. 2

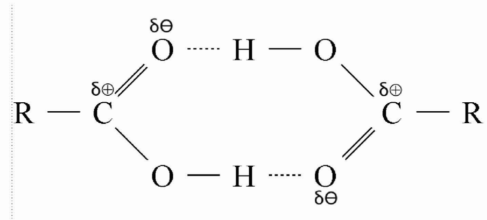

FIGURE 4. Dimmer of carboxylic acid.

(c)), and also companied by color change of sample from white to yellow after reaction 2 h. It suggested that in the dissolving process of ester, hydrolization reaction of $-CO\text{-}OCH_3$ maybe occurred under the condition of the presence of water.

Weight loss analysis showed that high-grade saturated fatty acid cannot almost be dissolved in steam at 140 ˚C. This can be explained by its stable structure at the present experimental conditions. As indicated in Fig. 4, high-grade saturated fatty acid tend

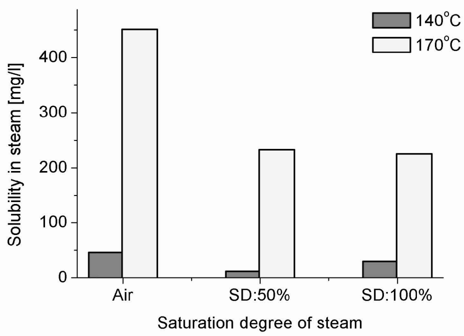

FIGURE 5. Solubility of myristyl alcohol at different steam saturation degree after reaction for 4h.

to get together to form a dimmer which was more stable than monomer itself.

Although different solubility in steam is directly relative with the boiling point of each tested compounds, it is considerably dependent on their chemical structures, for example, phenanthrene and palmitin acid, both have close boiling point but extremely different dissolving behavior in steam. In addition, effect of temperature was also not negligible. A higher temperature at 170 ˚C caused evaporation of alcohol more quickly than that at 140 ˚C. As shown in Fig. 5, solubility at 170 ˚C is eight times higher than that at 140 ˚C. It indicated increasing temperature is an important factor when considering improving the yield of alcohols in extraction industry. However, for ester and phenol, it wasn't thought to be so helpful as alcohol.

CONCLUSION

The experimental results showed that the dissolving behavior of each organic compound in steam is significantly different. Alcohols and phenanthrene can dissolve easily in steam with low density; Ester and phenol are unstable in saturated steam, as companied by a reaction of color change; Hydroquinone revealed a variable behavior characterized by an increase of weight at an early stage and a decrease later, which was thought to be water absorption and release process that is related to its polar chemical structure. Our experimental result showed that solubility of a compound is mainly influenced by its chemical functionality and the nature of the reaction medium. Medium composition, medium density, and temperature affected medium solvent power. It suggested the presence of more water must inhibit the evaporation of organic compounds, and more cause some complicated chemical reaction, such as oxidation and hydrolization of organic compounds.

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