



## Effective Recovery of Acetic Acid from Wood Vinegar by Reactive Distillation using Tungstophosphoric Acid-Active Carbon Catalyst

SHUANGMING LI<sup>1,2</sup>, XUEJIAO YANG<sup>1</sup>, JIAXIANG CHEN<sup>1</sup>, XIUJUAN WANG<sup>1</sup>, WENXIU LI<sup>2</sup> and SANSAN YU<sup>2,\*</sup>

<sup>1</sup>College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang 110142, P.R. China

<sup>2</sup>Key Laboratory of Chemical Separation Technology of Liaoning Province, Shenyang University of Chemical Technology, Shenyang 110142, P.R. China

\*Corresponding author: Tel./Fax: +86 24 89383730; E-mail: [yu.sansan@gmail.com](mailto:yu.sansan@gmail.com)

Received: 4 November 2013;

Accepted: 19 March 2014;

Published online: 30 September 2014;

AJC-16126

The recovery of acetic acid from wood vinegar by reactive distillation using tungstophosphoric acid-active carbon as catalyst has been studied. Methyl acetate is obtained as esterification product at the top of column. The loading capacity of tungstophosphoric acid on active carbon was optimized using batch distillation. In addition, the influence of various factors such as feed flow rate, MeOH vapor rate, rectifying section height and reflux ratio, on the conversion rate of acetic acid were investigated by using a model solution. A 71.94 % recovery of acetic acid is obtained from wood vinegar under the following optimal conditions: loading capacity 33 %, feed flow rate 60 g/h, MeOH vapor rate 114 g/h, rectifying section height 250 mm and reflux ratio 9:1.

**Keywords:** Reactive distillation, Acetic Acid, Wood vinegar, Tungstophosphoric acid, Recovery

### INTRODUCTION

Wood vinegar, a kind of brownish-black liquid, is generated in the process of charcoal production. The major constituent of wood vinegar is water, which makes up as much as 90 %. In addition to water, more than 200 organic compounds are included in smaller quantities, such as acetic acid, formaldehyde, acetone, methanol, tar and so on<sup>1,2</sup>. In many cases, acetic acid makes up about 90 % of total organic constituents. A large number of wood vinegar is being produced and discarded every day from the charcoal plant, which causes serious waste of acetic acid and environmental pollution. Therefore, it is very important and urgent to recover acetic acid from the acidic water.

It is difficult to separate acidic acid from water due to the miscibility between acidic acid and water. So far, some separation methods are applied to recovery diluted acid from industrial or medicine waste water, including ordinary distillation, azeotropic distillation, extractive distillation, solvent extraction and complexation extraction<sup>3-9</sup>. However, there are many disadvantages, such as low extraction yield, high cost and use of toxic organic solvents, limiting their application in industrial process.

Reactive distillation (RD), an effective separation method, combines the chemical reaction and the distillative separation of the product mixture in a single column. It is receiving increasing attention due to the elimination of chemical equilibrium

limitations, improved selectivity and increased process efficiency. In addition, a reactive distillation method can also reduce the costs of investments and operations obviously. It has been reported by some researchers that reactive distillation can be used for recovery of organic acid from aqueous solutions<sup>10-14</sup>. In these processes, catalysts play the important role and affect the efficiency and the cost directly. Ion exchange resins and zeolite were the catalysts used commonly to deal with 5-30 % acidic acid solutions<sup>13-16</sup>.

Heteropolyacids, a kind of polynuclear complexes containing an oxygen bridge, are frequently used as a re-usable acid catalyst in many chemical reactions<sup>17,18</sup>. In addition of strong acidic ability, heteropolyacids also possess of stable structure and good heat resistance, which was more applicable to industrial process. Therefore, the aim of this investigation was to recover acidic acid from wood vinegar to synthesize methyl acetate by using reactive distillation with tungstophosphoric acid as catalyst.

### EXPERIMENTAL

Wood vinegar, containing approximately 10 % acidic acid, was obtained from wood processing plants (Fushun, Liaoning, China). CH<sub>3</sub>COOH, HCl and CH<sub>3</sub>OH of analytical grade, H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub>·XH<sub>2</sub>O and activated carbon (20-40 mesh) were purchased from Guoyao Group Chemical Reagent Shenyang Co., Ltd. and distilled water was used in all experiments.

10 % acidic acid aqueous solution was prepared firstly as a simplified model solution, which was used as the feedstock in the following optimization process.

**GC analysis:** GC analysis of the products of reactive distillation was carried out on a GC7900 gas chromatograph (Shanghai Techcomp Bio-equipment Ltd., China) with a Porapak Q packed column (3 mm × 2 m) equipped with a TCD detector. GC was operated with the auto injection of 0.4 μL. Both the injector and the detector temperatures were 150 °C. The oven temperature was 120 °C for 11 min and then increased to 180 °C at a rate of 25 °C/min. The retention times of all the individual compounds were verified using authentic samples. Area correction normalization method was used for quantitative analysis of the chemical concentration.

**Preparation of tungstophosphoric acid-active carbon catalysts:** The preparation of tungstophosphoric acid-active carbon catalysts was carried out as following steps. Firstly, a certain amount of activated carbon was treated with diluted HCl solution to remove the alkaline substances on its surface. Activated carbon was then filtrated and washed several times with deionized water until there is no Cl<sup>-</sup> in the eluent. After being dried at 120 °C for 2 h, a certain amount of activated carbon was added into H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub> solution, which was then heated under reflux for 3.5 h. Unloaded H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub> was cleared with water. Tungstophosphoric acid-active carbon catalysts were obtained after being drying at 120 °C. Activation of the catalysts at 150 °C for 2 h was carried out before being used.

**Reactive distillation apparatus and process:** The reactive distillation experiments were carried out in a column with vacuum jacket, which included stripping section (250 mm), reaction section (500 mm) and rectifying section (100-450 mm). All the inner diameter of three parts was 20 mm. The stripping section and rectifying section were embedded with glass packing (3 × 16 mm), while the reaction section was embedded with staggered mixture of glass packing and Tungstophosphoric acid-Active carbon catalysts-containing metal gauze bag. Average loading of the catalyst for each catalyst bag was about 1.8 g.

This device was operated with a semi-continuous form, in which excessive methanol was charged into the bottom of the column one time. Reboiler was then heated for a certain time until the reflux was stable. After that, acidic acid aqueous solution was fed into the column at the top of reaction section continuously. Countercurrent contacting between methanol and acidic acid happened on all the trays through the column. At the top of rectifying section, methyl acetate was withdrawn under certain reflux ratio along with water and unreacted methanol. In the whole process, the column was insulated with fiber glass to minimize heat losses.

## RESULTS AND DISCUSSION

**Optimization of loading capacity:** Loading capacity of H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub> on activated carbon was a key variable for reactive distillation. The effect of catalyst loading on the conversion of acidic acid was investigated firstly in batch distillation under the condition of Mol(MeOH)/(CH<sub>3</sub>COOH) 2:1, temperature 70 °C and reaction time 3 h. Fig. 1 showed that 33 % catalyst loading gave the best conversion rate (96.26 %) of acidic acid.

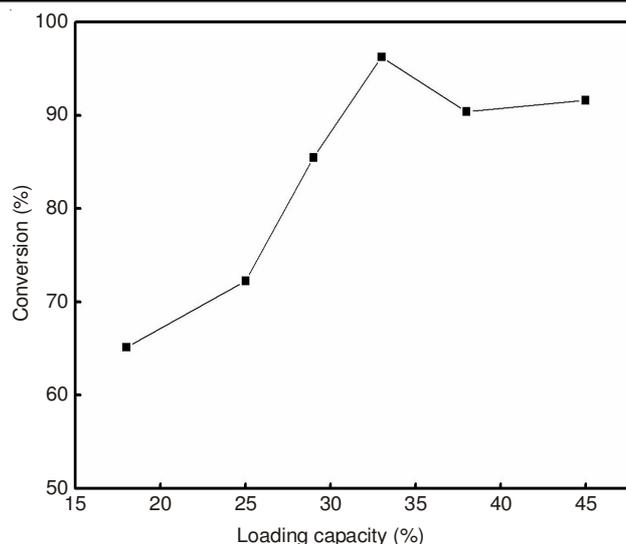


Fig. 1. Influence of PW<sub>12</sub> loadings capacity on the conversion of acidic acid

Between the ranges of 18-33 %, the conversion rate increased linearly with the increasing of catalyst loading. More catalyst loading (38 and 45 %), however, resulted in a decline in conversion rate. Adsorption of H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub> on activated carbon was physical adsorption, namely multi-molecular adsorption, in which, excessive loading capacity could not increase the catalytic performance when single molecular adsorption is saturated. Thus, 33 % was determined as optimal catalyst loading capacity in the following semi-continuous reactive distillation.

It was well known that the special Keggin structure was needed for the activity of H<sub>3</sub>O<sub>40</sub>PW<sub>12</sub>. Therefore, IR was applied to determine the retention of Keggin structure after being loaded on the carbon. Fig. 2 depicted the comparison of the IR spectrum of PW<sub>12</sub> before and after being loaded on activated carbon. It could be observed from Fig. 2 that four peaks of 1080, 980, 890 and 805 cm<sup>-1</sup> were responsible for P-Oa, W-Od, W-Ob-W and W-Oc-W, respectively, which indicated the Keggin structure still existed in tungstophosphoric acid-active carbon catalysts.

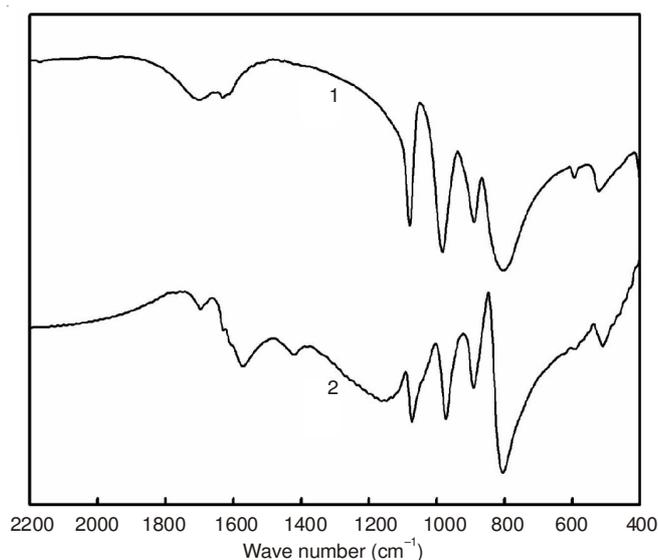


Fig. 2. IR spectrum of PW<sub>12</sub> before (1) and after (2) being loaded on activated carbon

**Effect of feed velocity on reactive distillation:** Fig. 3 showed the results obtained at five levels (30, 45, 60, 75 and 85 g/h) of aqueous solution of acidic acid feed velocity under the conditions of rectifying section height 250 mm, reflux ratio 11:1 and rising steam quantity 114 g/h. As shown in Fig. 3, the conversion was highest (80.52 %) when the feed velocity was 30 g/h. A downward trend of acidic acid conversion presented when the feed velocity increased from 45 to 85 g/h, which was caused by the decreased contact time on tungstophosphoric acid-active carbon catalyst. While the concentration of methyl acetate increased in the withdrawn fraction. Taking into account the processing capacity and effectiveness, 60 g/h was chosen as the optimal feed velocity for wood vinegar.

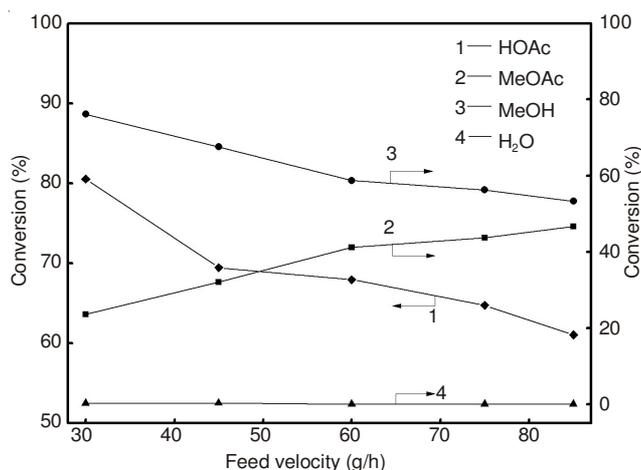


Fig. 3. Effect of diluted acidic acid feed velocity on reactive distillation, 1 conversion of HOAc; 2, 3, 4 the distillate composition of MeOAc, MeOH and H<sub>2</sub>O

**Effect of methanol vapor velocity on reactive distillation:** Methanol vapor velocity was also investigated under the conditions of rectifying section height 250 mm, reflux ratio 11:1 and acidic acid aqueous solution feed velocity 60 g/h. Results obtained were presented as Fig. 4, which indicated that the conversion increased from 58.44 to 72.07 % in the given range of 84-175 g/h of MeOH vapor velocity. While the concentration of methyl acetate decreased from 55.16 to 28.24 %. This result was consistent with the study of Sandesh *et al.*<sup>19</sup>, in which, it was explained that the increasing of MeOH vapor velocity could change the hydrodynamic behaviour of the gas-liquid system. A compromise result of 67.96 % for conversion rate and 41.26 % for methyl acetate concentration was obtained at 114 g/h.

**Effect of rectifying section height on reactive distillation:** Fig. 5 presented the influence of rectifying section height on the reactive distillation in the conditions of acidic acid aqueous solution feed velocity 60 g/h, MeOH vapor rate 114 g/h, reflux ratio 11:1. It showed that the conversion of acidic acid was affected greatly by rectifying section height and the highest conversion rate (67.96 %) was obtained at 250 mm. For withdrawn product, the concentration of methyl acetate increased slightly, while MeOH decreased with the increasing of rectifying section height. Overall, there was little change for the composition of top withdrawn, which might be caused by the excessive methanol and the similarity of boiling point between

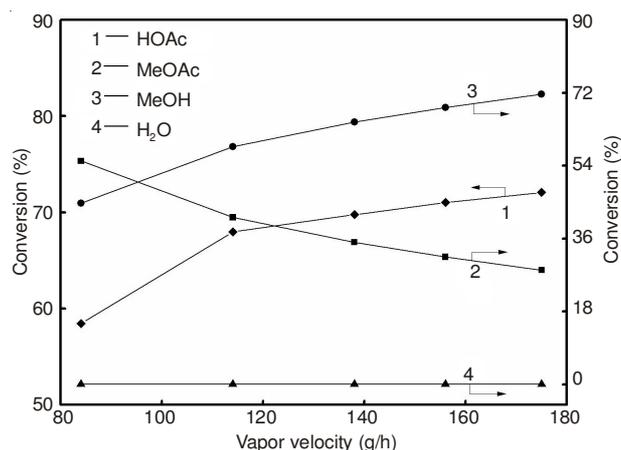


Fig. 4. Effect of MeOH vapor velocity on RD, 1 conversion of HOAc; 2, 3, 4 the distillate composition of MeOAc, MeOH and H<sub>2</sub>O

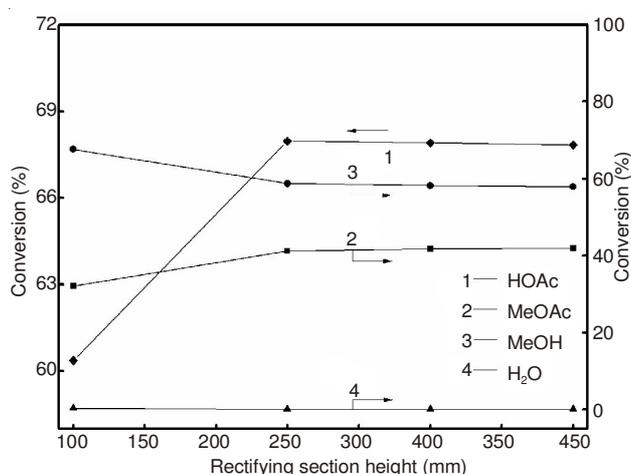


Fig. 5. Effect of rectifying section height on reactive distillation. 1 conversion of HOAc; 2, 3, 4 the distillate composition of MeOAc, MeOH and H<sub>2</sub>O

alcohol and ester. Therefore, 250 mm was selected as the optimal rectifying section height.

**Effect of reflux ratio on reactive distillation:** Reflux ratio was also optimized under the conditions of acidic acid aqueous solution feed velocity 60 g/h, MeOH vapor rate 114 g/h, rectifying section height 250 mm and the result was presented in Fig. 6. As shown in Fig. 6, a continuing decline (from 74.57 to 62.04 %) of conversion appeared with the increasing reflux ratio. Alcohol and ester concentration achieved the minimum value (58.69 %) and the maximum (41.26 %), respectively at the reflux ratio 11:1. It indicated that increasing reflux ratio could enhance separation efficiency, however, reduce the withdrawing rate, which inhibited the positive reaction greatly. Process efficiency being considered, 9:1 was selected as the optimal ratio.

Under a certain reactive distillation condition, a balance should be established firstly before withdraw from the top. Therefore, the time required to form a stable state in reactive distillation was studied in this paper. It could be seen from Fig. 7 that the top temperature and the concentration of methyl ester in withdrawn product achieved a balance in 60 min. The top temperature and the concentration of methyl ester were 58.2 °C and 41 %, respectively.

TABLE 1  
CONVERSION RATE OF ACETIC ACID IN WOOD VINEGAR AND THE OVERHEAD COMPONENT ANALYSIS

No.	Conversion of CH <sub>3</sub> COOH %	Top withdraw composition Wt%			
		Methyl acetate	H <sub>2</sub> O	CH <sub>3</sub> OH	Methyl propionate
1	71.85	41.03	0.51	56.76	1.70
2	72.03	41.40	0.33	56.67	1.60
3	71.94	40.95	0.39	57.02	1.64
Mean value	71.94	41.12	0.41	56.82	1.65

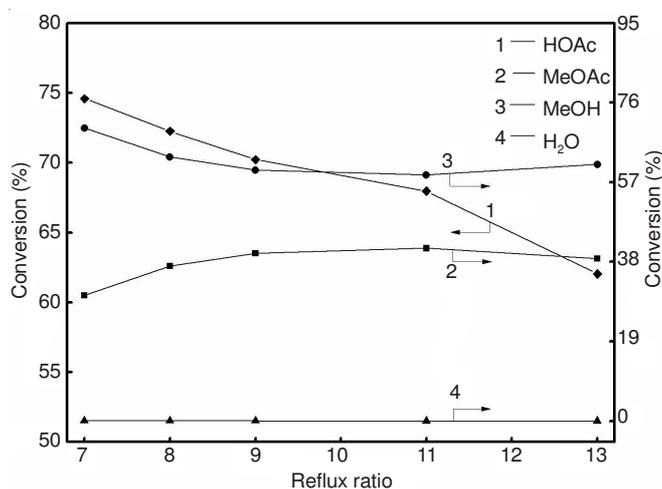


Fig. 6. Effect of reflux ratio on reactive distillation, 1 conversion of HOAc; 2, 3, 4 the distillate composition of MeOAc, MeOH and H<sub>2</sub>O

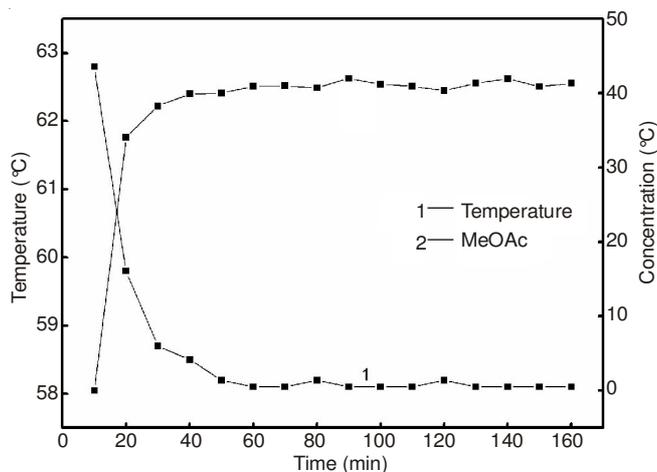


Fig. 7. Equilibrium curves between top temperature, methyl ester content and time

**Application of the method for wood vinegar:** The optimal method had been applied to recovery of acidic acid from raw wood vinegar under above optimized conditions. Withdrawn of the top product was started after 60 min. Three replications were carried out and the results were given in Table-1. It showed that the mean conversion of acidic acid was 71.94 % and the mean concentration of MeOAc, H<sub>2</sub>O and MeOH were 41.12,

0.41 and 56.82 %, respectively. In addition of methyl acetate, methyl propionate was also detected in the product with a concentration of 1.65 %.

## Conclusion

A reactive distillation method using tungstophosphoric acid-active carbon as catalyst was developed for the recovery of acidic acid from wood pyrolysis by-products called wood vinegar. Tungstophosphoric acid-active carbon catalyst was first prepared and then the loading capacity, feed flow rate, MeOH vapor rate, rectifying section height and reflux ratio were optimized. Optimal conditions were loading capacity 33%, feed flow rate 60 g/h, MeOH vapor rate 114 g/h, rectifying section height 250 mm and reflux ratio 9:1. Under this condition, the optimal conversion of 71.94 % was obtained.

## REFERENCES

- L.G. Wei, B.W. Lu, Y.C. Ma and Z.Y. Li, *Chem. Ind. Forest. Prod.*, **31**, 12 (2011).
- Y.X. Li and H.W. Lin, *J. Anal. Sci.*, **28**, 58 (2012).
- S.J. Wang and K.J. Huang, *Chem. Eng. Process.*, **60**, 65 (2012).
- H. Demiral and M.E. Yildirim, *Water Sci. Technol.*, **47**, 183 (2003).
- R.P. Bhatt and S.B. Thakore, *Int. J. Sci. Eng. Technol.*, **1**, 46 (2012).
- C.C.-H. Shin, J.-Y. Kim, J.-Y. Kim, H.-S. Kim, H.-S. Lee, D. Mohapatra, J.-W. Ahn, J.-G. Ahn and W. Bae, *J. Hazard. Mater.*, **162**, 1278 (2009).
- P. Kalaichelvi, M. Perumalsamy, A. Arunagirri and K. Sofiya, *J. Univ. Chem. Technol. Metall.*, **42**, 291 (2007).
- S.Y. Cheng and W. Huang, *Coal Chem. Ind. J.*, **5**, 9 (2010).
- V. Ragaini, C.L. Bianchi and C. Pirola, *Chem. Eng. J.*, **131**, 257 (2007).
- Z. Xu, A. Afacan and K.T. Chuang, *Can. J. Chem. Eng.*, **77**, 676 (1999).
- R. Kumar and S.M. Mahajani, *Ind. Eng. Chem. Res.*, **46**, 6873 (2007).
- W.-J. Hung, I.-K. Lai, Y.-W. Chen, S.-B. Hung, H.-P. Huang, M.-J. Lee and C.-C. Yu, *Ind. Eng. Chem. Res.*, **45**, 1722 (2006).
- Z.G. Zhang, X.F. Li, S.M. Xu and X.G. Li, *Tianjin. Univ.*, **12**, 264 (2006).
- A. Singh, A. Tiwari, S.M. Mahajani and R.D. Gudi, *Ind. Eng. Chem. Res.*, **45**, 2017 (2006).
- T. Suman, S. Srinivas and S.M. Mahajani, *Ind. Eng. Chem. Res.*, **48**, 9461 (2009).
- Y.H. Li, S.B. Yu, X.G. Yuan and H. Wang, *Ind. Eng. Chem. Res.*, **41**, 4936 (2002).
- Y. Li, W. Chu, M.H. Chen and J.Y. Hu, *J. Wuhan, Univ. Technol. (Mater. Sci. Ed.)*, **2**, 234 (2008).
- H. Atia, U. Armbruster and A. Martin, *Appl. Catal. A*, **393**, 331 (2011).
- K. Sandesh, P.E. JagadeeshBabu, S. Math and M.B. Saidutta, *Ind. Eng. Chem. Res.*, **52**, 6984 (2013).