

# Practical Study of Purification of Lao Cai Wet Process Phosphoric Acid, Based on Tributyl Phosphate (TBP) – Kerosene Mixture Solvent Extraction

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## Abstract

*The purification of wet process phosphoric acid using solvent extraction has been widely applied at industrial scale. However, the performance of the purification depends strongly on the solvent characteristics. Common solvents used for the extraction are butanol, hexanol, tributyl phosphate (TBP) and MIBK mixture, ... in which TBP/Kerosene have proved to be one of the the most efficient solvent mixture. In this work, the effects of temperature, solvation heat, mixing time, and organic/aqueous phase ratio on the extraction of Lao Cai wet process phosphoric acid was studied. The obtained results from experiments that have true potential to apply in the industrial manufacturing process.*

Keywords: liquid-liquid extraction, wet phosphoric acid, Tributyl phosphate, TBP, Kerosene

## 1. Introduction

Phosphoric acid has widely used in chemical industry, especially in the food industry. The demand of highly pure phosphoric acid has been increasing remarkably in recent years. In general, phosphoric acid is manufactured by two major processes: wet process and thermal process. The raw material for the thermal process is phosphorus, which is produced from apatite ore in the arc furnace. Phosphorus is then oxidized and hydrated to obtain phosphoric acid [1, 2]. The acid produced by the thermal process has a much higher purity, essentially containing only the phosphatic value. However, this process consumed too much energy that made its cost increased significantly in the last ten years. In practical industry, the cost of raw material, yellow phosphorus, accounting for 95,5% total production cost. Moreover, the price of coke and electricity has risen, and the basic investment capital for thermal process phosphoric acid has climbed simultaneously. So this process has been gradually limited and tended to decrease because of its large energy consumption and environmental impact problems.

Wet process phosphoric acid (WPA) is produced based on a reaction between phosphate ore and a mineral acid, usually sulfuric acid. Phosphoric acid obtained from the wet process contains inorganic and organic contaminants present in the raw materials with a variable concentration depending on the crude phosphate origin and its pretreatment [3]. Several techniques are employed to refine the acid from the

crude WPA for food or technical grade acids such as solvent extraction, paramagnetism, electro dialysis, electrodeposition and electrode ionization on ion exchange textiles [4]. However, solvent extraction has been widely employed in the commercial processing line of the food and technical grade phosphoric acid all over the world. Moreover, the advantages of this technique have been proved on recovery any of valuable elements from the raffinate as an added value to the solvent extraction process. This method is not only easy in operation, but also cost effective. In this study, the solvent extraction method was selected for the purification of WPA. The process consists of three major steps: (1) the solvent was added to separate phosphoric acid from the feeding acid by liquid-liquid extraction, (2) purified acid was recovered by water, and (3) the solvent was also reverted for the circulation in the purification process.

Laila A. Guirguis et al. studied the purification process of crude phosphoric acid by TBP/Butanol mixture in a single stage extraction process. In their work, separation efficiency has achieved of 43% [4]. The work of Moussa Alibrahim [5] showed that Kerosene gives the highest extraction yield with TBP in WPA purification compared to the other diluents such as benzene, toluene and chloroform. In another study, Laila A. Guirguis et al. [6] also purified  $H_3PO_4$  by a mixture of hydrophobic and hydrophilic solvent extraction in a single stage extraction from crude phosphoric acid containing 57,75%  $P_2O_5$ . The hydrophilic and hydrophobic solvents they were used

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in their research namely methanol and hexanol. The phosphate containing components were distributed in high molecules weight alcohol fraction while the impurities were segregated to low molecules weight alcohol fraction. The optimum ratio for the extraction mentioned in the work was five parts of methanol, one part of fed acid and four parts of hexanol. Using the proposed ratio, the recovery of 95% was achieved however, methanol/hexanol solvent mixture were rarely used in industrial scale. Mohamedalkhaled Abdulbake et al. [7] studied the synergistic effect of some alcohols on the extraction of  $H_3PO_4$  from Syrian WPA by Tributyl Phosphate (TBP). The results showed that the stirring time does not cause a significant effect on extraction which indicates that extraction is not diffusion controlled. Besides, it also showed the negative effect of temperature on the extraction of  $H_3PO_4$  but in the stripping, temperature has positive effect. The separation time for the extraction by TBP with alcohols as diluent is smaller than that by TBP with kerosene at the phase ratio O/A = 5/1. Furthermore, Hannachi Ahmed et al. [8] had a study on the purification of WPA by solvent extraction with a mixture of TBP and MIBK (methyl isobutyl ketone). They stated that the order of selectivity for the extraction is MIBK < solvent mixture of TBP and MIBK < TBP.

In the present study, the solvent extraction of Lao Cai WPA is addressed and the effects of temperature, mixing time, solvation heat and the Organic/Aqueous phase ratio on the process efficiency are also analyzed.

## 2. Experiments

### 2.1. Materials

- The main and starting material for the present work is a commercial WPA containing 48,9%  $P_2O_5$  which is supplied by Duc Giang – Lao Cai chemicals joint stock company, Tang Loong Industrial zone, Tang Loong, Bao Thang, Lao Cai.
- TBP: 98%; density  $0,978 \pm 0,02$ ; color  $\leq 0,5$ .
- Kerosene (carbon chain: 6 – 16 C); density:  $0,775 - 0,840$  g/ml; viscosity at  $20^\circ C$ :  $< 8cSt$ ; autoignition temperature:  $220^\circ C$ ;  $T_{100} < 300^\circ C$ ; freezing point:  $< -50^\circ C$ .
- The reagents used in the experiments were of analytical grade quality and double-distilled water was used in all preparations.

### 2.2. Instrumentations

- A Shimadzu 160 A Double beam UV spectrophotometer with a wavelength range of

200-1100 nm is used for spectrophotometric determination of sulfate, phosphate and total rare earth elements.

### 2.3. Analysis Procedures:

#### 2.3.1. Analytical procedures:

Many chemicals and instrumental analysis methods were used for the quantitative determination of major, minor and trace elements of the present phosphoric acid, according to ISO 6353-2:1983 - Reagents for chemical analysis - Part 2: Specifications.

#### 2.3.2. Extraction analysis:

Extraction was carried out in a beaker with a paddles blades stirrer placed in a thermostat to control the temperature. Given amounts of each of the aqueous and organic phases were mixed during a determined time period and then liquid-liquid phase separation process was carried out in a separating funnel.

The concentration of  $P_2O_5$  in the aqueous phase was determined by the citroammonium molybdate method, whereas the concentration of  $P_2O_5$  in the solvent was calculated from the material balance.

The distribution ratio (D) was calculated from equation (1):

$$D = [P_2O_5]_{\text{organic}} / [P_2O_5]_{\text{aqueous}} \quad (1)$$

where:  $[P_2O_5]$  = weight percent of  $P_2O_5$ .

The extracted  $P_2O_5$  content (%E) was calculated from the equation (2):

$$\%E = 100 D (P) / [1 + (P) D] \quad (2)$$

Where: P (phase ratio) is value of organic / value of aqueous (or O/A)

D: the distribution ratio

The degree of phase separation with respect to time was determined by measuring the change of height level from the phase interface to the bottom of the column.

## 3. Results & Discussion

### 3.1. Chemical analysis:

The analyzed composition of raw WPA produced at Lao Cai chemicals joint-stock company is shown in Table 1:

**Table 1.** Chemical analysis of industrial grade phosphoric acid.

No.	Property	Unit	Result	Method
1	Total P <sub>2</sub> O <sub>5</sub>	%(m/m)	48,9	ISO 3706:1976 (Quinoline Phosphomolybdate Gravimetric method)
2	CaO	%(m/m)	0,04	ISO 3706:1976 ICP
3	MgO	%(m/m)	0,59	ISO 3706:1976 ICP (MOD)
4	Fe <sub>2</sub> O <sub>3</sub>	%(m/m)	1,98	ISO 6353/2:1983 ICP
5	Al <sub>2</sub> O <sub>3</sub>	%(m/m)	3,19	ISO 3706:1976 ICP (MOD)
6	Fluoride (F)	%(m/m)	0,54	FCC 8-Fluoride Limit Test-ISE III
7	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	%(m/m)	3,67	IS 798-1986
8	Total suspended solid content	%(m/m)	1,87	Ref. ISO 11923:1997
9	Arsenic (As)	ppm	15,1	AOAC 2012 (2013/06)/ICP
10	Chloride (Cl)	ppm	<20	ISO 6227:1982
11	Density at 30°C	Kg/L	1,702	ASTM D-4052-15
12	Chromium (Cr)	ppm	42,9	ISO 6353/2-1983/TCP (MOD)
13	Cadmium (Cd)	ppm	<1	ISO 6353/2-1983/TCP (MOD)
14	Titanium (Ti)	ppm	136	ISO 6353/2-1983/TCP (MOD)
15	Nikel (Ni)	ppm	24,8	ISO 6353/2-1983/TCP
16	Molybdenum (Mo)	ppm	1,66	ISO 6353/2-1983/TCP (MOD)
17	Vanadium (V)	ppm	31,6	ISO 6353/2-1983/TCP (MOD)
18	Lead (Pb)	ppm	7,5	ISO 6353/2-1983/TCP
19	Mercury (Hg)	ppm	Not detected (LOD 0,01ppm)	US EPA 7470A:1994 (NIC Mercury Analyzer-WA-5A)

Remark: - The analyses have been performed in accordance with latest issues of the relevant test methods unless otherwise stated;

- Precision parameters apply to the determination of above test results. Also refer to ASTM 3244, IP 367 and Appendix E of IP Standard Method of analysis and testing for utilization of test data to determine conformance with specifications;

- %(m/m) = %(w/w) = wt% = %mass; mg/kg = ppm(m/m) = ppm mass = ppm(w/w) = ppm wt;

- LOD: Limit of detection.

### 3.2. Effect of temperature on the extraction process

Effect of temperature on the extraction process was studied. Four experiments at different temperatures were performed with O/A (organic/aqueous) ratio of 5/1. The organic solvent used was TBP/Kerosene mixture at ratio TBP/Kerosene of 6/4. The mixing time and settling time was set to 3 and 5 minutes, respectively. Stirring speed of 400 rpm was used at the mixing stage. The results obtained from the experiments showed that as the temperature increased the extraction efficiency (%E) was decreased. In this work, the effective temperature for the extraction process was 32°C as illustrated in Fig.1.

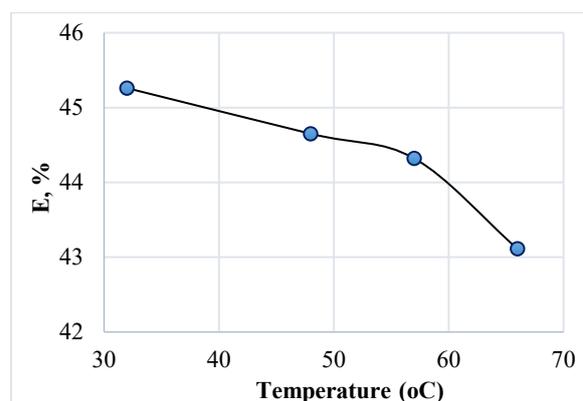
The relation between the equilibrium constant K and the temperature is given by Van Hoff's equation [1]:

$$d \ln K / dT = \Delta H / R.T^2$$

where R is gas constant (R = 8,314 J/mol-K)

By integration, K is calculated by:

$$\ln K = (-\Delta H / R) (1 / T) + a$$



**Fig. 1.** Effect of temperature on the extraction efficiency (%E).

Since the distribution ratio  $D$  is related by definition to the equilibrium constant  $K$  the previous equation could be written as follows:

$$\ln D = (-\Delta H / R) (1 / T) + a$$

The experimental results are plotted in Fig.2 where  $\ln D$  is considered as a function of  $1000/T(^{\circ}K)$ . Using linear regression, it is possible to calculate  $\Delta H = -2013 \text{ J/mol}$ .

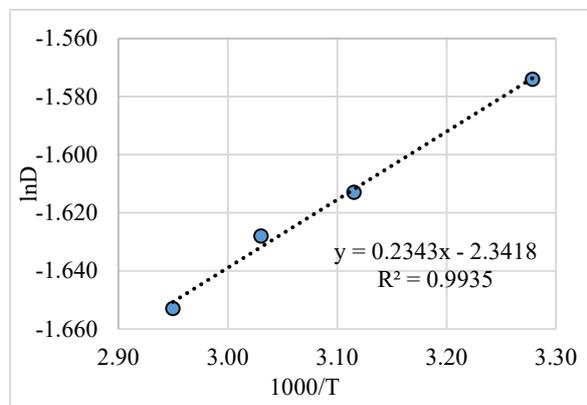


Fig. 2. Effect of temperature on the distribution ratio.

### 3.3. Effect of solvation heat on the process mixture temperature

Effect of solvation heat on the phase mixing process was conducted at O/A (organic/ aqueous) ratio of 5/1 by the solvent mixture TBP/Kerosene with the ratio of 6/5. The stirring speed was set to 370 rpm. Solvent and crude acid were initially input at room temperature ( $32^{\circ}C$ ) and the mixing temperature variation is monitored continuously throughout the experiment. The total time of phase mixing was 180 seconds. The mixing temperature profile obtained from the measurement was depicted in Fig.3.

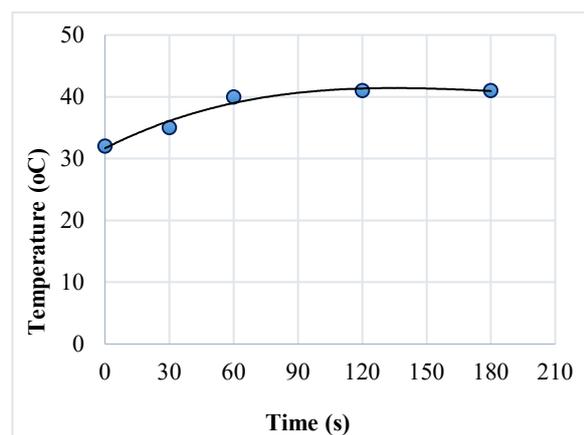


Fig. 3. Effect of phase contact time on the mixture temperature

According to the experimental results, it is possible to noticed that the solvation heat has a small effect on extraction.

### 3.4. Effect of stirring time on the extraction process

Effect of the mixing time on the extraction process was examined at O/A (organic/aqueous) phase ratio of 5/1 using TBP/Kerosene mixture with ratio of 6/4. The settling time was set to 5 minutes and the stirring speed was set to 370 rpm. Initial temperature of Solvent and crude acid was  $32^{\circ}C$ . Experimental data of extracted  $P_2O_5$  content (%E) as a function of mixing time are shown in Fig.4. It can be stated from the measurement that the effective stirring time is 60 seconds.

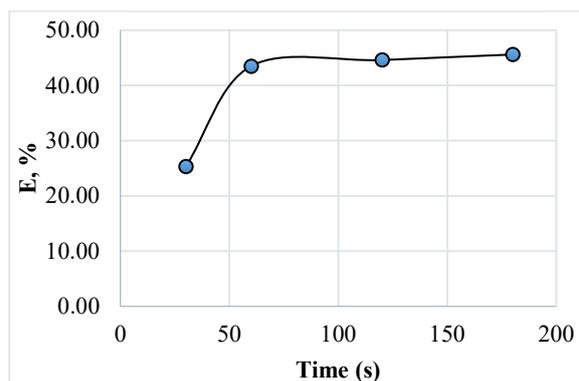


Fig. 4. Effect of stirring time on the extraction efficiency (%E).

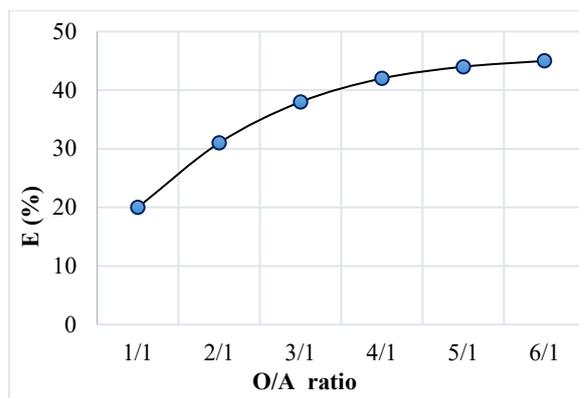


Fig. 5. Effect of organic/aqueous phase ratio on the extraction efficiency (%E).

### 3.5. Effect of organic/aqueous phase ratio (O/A) on the extraction process

Six different organics to aqueous phase ratios namely 1/1, 2/1, 3/1, 4/1, 5/1 and 6/1 were used to figure out the proper phase ratio for extraction of  $P_2O_5$  from the feeding WPA. The remaining operation parameters are kept as mentioned before. The measured data of the extraction efficiency (%E) with respect to O/A ratio are given Fig.5. Regarding to the combined effects of other operating parameters, as the O/A ratio increased, effect of the process rose. But the rise step of effect increased become smaller.

Additionally, when O/A ratio using is big enough, the productivity of the purification process therefore so small. Thus, due to the change of effect on extraction process is insignificant, the appropriate organic to aqueous phase ratio could be taken as 5/1.

#### 4. Conclusions

At low temperature (below 60°C), the extraction is slightly influenced by temperature, however, when the temperature goes higher, extraction percent is decreased. Therefore, one can prove that the temperature has a small negative effect on the extraction process and room temperature could be an appropriate operating parameter of the extraction.

The solvation heat has a small effect on extraction, which indicates that extraction is considered to be mixing controlled rather than diffusion controlled.

The effective time interval for the mixing step is 60 seconds and the cost-effective organic to aqueous phase ratio is 5/1.

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