Study for the degumming pretreatment of rubber seed oil

X Y Li¹, Y B Chen¹-², X Zhang¹, D Souliyathai¹, S P Yang¹ and Q Wang¹

¹School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan, PR China

E-mail: c20072007@163.com

Abstract. With the rapid development of the aviation industry, appearing of the aviation carbon tax and the increasingly serious environmental problems have forced the world to research the development of renewable bio-aviation fuel. Renewable biological aviation fuel contains phosphorus that could reduce the synthesis of noble metal catalysts such as Pd, Pt activity. In order to get low content of phosphorus in degummed oil of non-edible vegetable oil, in this paper, with rubber seed oil as raw material, making the experiment of single factor at the influence of temperature, stirring speed, adding amount of monoethanolamine (MEA) and water amount. The experimental results show that the added amount of MEA is 2.5% in the weight of oil, and temperature is 60 ℃, while the amount of added water is 2% in the weight of oil, reaction time is 40 min, and stirring speed is 200 r/min. Under these conditions, the phosphorus content of rubber seed oil can be reduced to below 3 mg/kg, degumming rate is 91.37%, and the degumming effects are obvious, which also provides some foundation for follow-up studies.

1. Introduction
With the development of the global economy, air transport occupies an important position and the growth rates of air and cargo air freight have arrived at 4.9% and 5.3% [1]. At the same time, the aviation industry is under double pressure to reduce greenhouse gas emissions and resource shortages [2]. At present, countries have carried out research on biomass energy, and searching for renewable bioaviation kerosene has become a hot topic in the research of scientists. With the oil of animals and vegetables as raw materials, the bio-aviation fuel technology with hydrogen treatment owns a simple process and a high maturity [3], the raw materials that China uses to prepare for bio-aviation fuel is mainly non-edible oil.

The oil that is not degummed with vegetable oil usually contains colloid, and most of it is phospholipid. The presence of phospholipids makes the oil bubbling while heating the oil, and the phospholipid becomes bitter, moreover, during the storage process, phospholipid can be easily rancid [4]. At high temperature, phospholipids produce confocal phenomena, so before entering the deodorization, it is required that the phosphorus content be less than 10 mg/kg, and it is ideal that the content of primary oil phosphorus is less than 5 mg/kg after refining [5].

In the preparation of bio-aviation fuel, the cost of raw materials accounts for more than 60% of the total [6]. Phosphorus in phospholipids seriously affects the performance and repeated use of precious metal catalysts, therefore, non-edible vegetable oil degumming pretreatment is an important part in the preparation of biofuel. At present, the degumming method mainly includes water degumming, acid degumming, enzymatic hydrolysis, membrane filtration, etc. Jiang X F and others [7] studied the
technological conditions for the degumming of rapeseed oil, drawing a conclusion through response surface optimization: temperature 60℃, 50% citric acid content accounted for 0.22% of oil weight, water adding amount 3.34% of oil weight, the degummed rapeseed oil phosphorus content is 15.67 mg/kg when acid treatment time was 24.78 min, degumming rate was 93.76%. Wu Y J and others[8] studied for the cold pressed sesame oil with degumming acid method, taking the orthogonal experiment to optimize the best experimental conditions: the dosage of acid is 0.5%, temperature is 60℃, water content is 2.5%, and the reaction time is 45 min. In this condition, the phospholipid content of the degummed oil was 54.05 mg/kg and the stripping rate reached 72.9%.

In this paper, rubber seed oil is used as raw material, and on the basis of the existing acid method degumming, the defect of the acid method is not completely, MEA reagent was introduced in the process of degumming, the influence of various factors and the better experimental conditions are determined to provide references for further amplification experiments.

2. Materials and methods

2.1. Experimental raw materials
The rubber seed oil is produced in Pu'er, Yunnan province and its main properties are shown in table 1.

Table 1. The raw material oil properties.

| material      | Phosphorus content/mg/kg | Acid value/mgKOH/g | Saponification value/mgKOH/g | Iodine value/g/100g |
|---------------|--------------------------|--------------------|-------------------------------|----------------------|
| rubber seed   | 34.76                    | 38.57              | 186.64                        | 159.58               |

2.2. Experimental methods

2.2.1. Preparation of rubber seed degumming oil. The preparation of rubber seed degumming oil mainly includes the following steps: I. The untreated rubber seed oil is heated in the setting temperature; II. Adjust the stirring speed, add MEA and deionized water to stir the reaction; III. After processing, cool to room temperature, then centrifuge separation; IV. After dehydration, get the oil of degummed. The experimental device is shown in figure 1.

![Figure 1. Experimental device diagram.](image)

1. Experimental station; 2. JJ-1A digital display electric mixer controller; 3. Thermostatic water bath pan; 4. Water; 5. Triangular conical flask; 6. The oil; 7. Electric mixer motor

2.2.2. Single factors experiment design. Taking the temperature, stirring speed, adding amount of monoethanolamine (MEA), water amount and MEA processing time as variables, set 5 factors 5 levels and set 3 parallel experimental schemes for each level, to research the effects of each factor on phosphorus content in rubber seed oil degumming. The specific experimental parameters [7]: the temperature (40-80℃), stirring speed (100-300 r/min), added amount of monoethanolamine (MEA)
(1%-3%) of oil weight, water amount (1%-5%) of oil weight and MEA processing time (10-50 min).

2.2.3. Determination method. The phospholipid fore and after content the rubber seed oil degumming can be determined by GB/T 5537-2008 [9]. The calculation formula as follows:

\[
X = \frac{P}{m} \times \frac{V_1}{V_2} \times 26.31
\]

In the formula: \(X\), the content of phospholipids measured, mg/g; \(P\), the corresponding amount of phosphorus in the standard curve, mg; \(m\), oil quality, g; \(V_i\), the volume of diluted after sample ash, mL; \(V_2\), the volume of the night being measured, mL; 26.31, the conversion coefficient between phosphorus content and phospholipid content.

The acid value was determined according to GB/T 5530-2005 [10]. The calculation formula is as follows:

\[
S = \frac{56.1 \cdot V \cdot c}{m}
\]

In the formula: \(S\), Untested oil acid value, mg(KOH)/g; \(V\), standard solution KOH volume, mL; \(c\), standard solution KOH concentration, mol/L; \(m\), oil quality, g; 56.1, KOH mole mass, g/mol.

The determination of the saponification value was determined according to the method of GB/T 5534-2008 [11]. The calculation formula is as follows:

\[
I = \frac{(V_0 - V_1) \times c \times 56.1}{m}
\]

In the formula: \(I\), to test the saponification value of oil, mg(KOH)/g; \(V_0\), blank standard solution HCl volume, mL; \(V_1\), titration of the standard solution HCl volume, mL; \(c\), standard solution HCl concentration, mol/L; \(m\), oil quality, g.

The determination of iodine value was determined according to GB/T 5532-2008 [12]. The calculation formula is as follows:

\[
W = \frac{12.69 \times c \times (V_1 - V_2)}{m}
\]

In the formula: \(W\), to test the Iodine value of oil, g/100g; \(c\), standard solution Na\(_2\)S\(_2\)O\(_3\) concentration, mol/L; \(V_1\), blank standard solution Na\(_2\)S\(_2\)O\(_3\) volume, mL; \(V_2\), titration of the standard solution Na\(_2\)S\(_2\)O\(_3\) volume, mL; \(m\), oil quality, g.

3. Experimental results and discussion

3.1. Results and discussion of single factor experiment

3.1.1. The influence of MEA addition on the content of phosphorus of rubber seed oil. At temperature of 60°C, added different amounts of MEA when the stirring speed is 200 r/min, at the same time, added the addition amount of 2% of the oil quality deionized water in the same temperature, continue to mixing process of 40 min then make centrifugal separation, take upper sample to determine phosphorus content, the result was shown in figure 2.

It can be seen from figure 2 that with the increasing of MEA addition, the phosphorus content of rubber seed oil decreased obviously. It is due to the rapid reaction of the phospholipid acid in the MEA reagent and oil to the phosphatidyl ethanolamine, which is easy to hydrate, leading to the rapid decrease of phosphorus content. When the addition of MEA was 2.5% of the oil weight, the addition of MEA was added, and the removal effect of phosphorus was not obvious, indicating that the phosphorus in rubber seed oil was mostly removed. Therefore, the best MEA addition to determine the experiment was 2.5%.
3.1.2. Experimental effect of temperature on phosphorus content of rubber seed oil. Under stirring speed of 200 r/min, added the MEA that is 2.5% of the weight of oil, at the same time, added the deionized water that was 2% of oil by weight with the same temperature, respectively dealt with under the temperature of 40-80℃ for 40 min then made centrifugal separation, take upper sample determination of phosphorus content, the result was shown in figure 3.

It can be seen from figure 3 that in a certain temperature range, the increase of temperature was beneficial to the removal of phosphorus, because the raised temperature was conducive to the formation and separation of colloidal particles. When the temperature reached 60℃, the phosphorus content dropped to the lowest, continue to raise the temperature, phosphorus content had a rising trend. It was because the temperature was higher than the gelatinous mass of the condensate which results in the dispersion of the colloid. Comprehensive consideration, it can determine the optimum degumming temperature was 60℃.

3.1.3. The influence of water added content on the rubber seed oil phosphorus analyzed. At the temperature of 60℃, stirring speed of 200 r/min, added the MEA that was 2.5% of the weight of oil, added the deionized water of different amount but same temperature, after 40 minutes of continuous mixing, the centrifugal separation was done. And the phosphorus content was determined by the upper sample, and the result was shown in figure 4.

It can be seen from figure 4 that in a certain range, the increase of water content is beneficial to the removal of phosphorus. When the amount of added water with deionized water temperature was 2% of oil weight, the phosphorus content was minimized. The increase of phosphorus content was not decreased but increased a little while adding water, which may be due to the emulsification of excess water, which results in incomplete phospholipid separation. The suitable amount of water can make the phospholipids fully hydrated and absorb other gelatin. The granules were enlarged and easily removed. The absorption of water by phospholipid can result in emulsification and degumming effects. Therefore, it was determined that the optimal water addition of degumming of the experiment was 2% of the oil weight.

3.1.4. The experimental effect of MEA treatment time on phosphorus content of rubber seed oil. At the temperature of 60℃, the stirring speed of 200 r/min, add the MEA that was 2.5% of the weight of oil, at the same time, add the deionized water that was 2% of oil weight with same temperature. Continuous to mixing processing, the centrifugation was carried out according to different processing time, and the phosphorus content was determined by the upper sample, and the result was shown in figure 5.
Figure 4. Effect of water addition amount on phosphorus content of rubber seed oil.

Figure 5. Effect of MEA treatment time on phosphorus content of rubber seed oil.

It can be seen from figure 5 that within 10-40 min, the phosphorus content gradually decreased with the increasing of MEA treatment time. When the treatment time of MEA was 40 min, the phosphorus content was minimized. Adding the MEA treatment time, the phosphorus content increased slightly. It was due to a certain amount of time to react with the phospholipid acid in the MEA reagent and oil. After a period of time, most of the phospholipids were converted to phosphatidyl ethanolamine, the MEA reagent no longer played a decisive role. The time was too long, the gelatinization and oil phase will occur local emulsification, resulting in a slight increase in phosphorus content. Comprehensively consideration, the best time to determine the experiment was 40 min.

3.1.5. The experimental effect of stirring speed on the phosphorus content of rubber seed oil. At the temperature of 60 ℃, added the MEA that was 2.5% of the weight of oil, at the same time, added the deionized water that was 2% weight of oil with the same temperature. Continuously, the centrifuge was separated after 40 min at different stirring speed, the phosphorus content was determined by the upper sample, and the result was shown in figure 6.

Figure 6. Effect of stirring speed on the phosphorus content of rubber seed oil.

As can be seen from figure 6, as the mixing speed increases, the phosphorus content starts to decrease obviously. It was due to the rapid reaction of the MEA reagent in the beginning that the rapid
precipitation of phosphatidyl ethanolamine, after which the phospholipid content was less, the change of phosphorus content tended to be gentle. When the speed reached 200 r/min, the phosphorus content was minimized. Therefore, it was determined that the optimal stirring speed of the experiment was 200 r/min.

4. Conclusions
The experimental conditions of single factor were obtained by using rubber seed oil as raw material: the results show that addition of MEA is 2.5% of the weight of oil, temperature is 60°C, the amount of added water is 2% of oil by weight, reaction time is 40 min, and stirring speed is 200 r/min. Under these conditions, the phosphorus content of rubber seed oil can be reduced to below 3 mg/kg, degumming rate is 91.37%, the degumming effect is obvious. It provides some basis for the subsequent non-edible vegetable oil degumming experiment.

Acknowledgments
This work is partial fulfillment of funded research program 21266032, financially supported by Natural Science Foundation of China.

References
[1] Sun X Y, Liu X, Zhao X B, et al 2013 Progress in synthesis technologies and application of aviation biofuels *Chinese J. of Biotechnol.* 29(3) 285-98
[2] Tao Z P 2011 Progress in alternative fuels for aviation and suggestions of ITS development in China *Petroleum Processing & Petrochemicals* 42(7) 91-6
[3] Zhao G H, Jiang W, Niu X Y, et al 2014 Jey fuel preparation technology and application prospects *Sino-global Energy* 19(8) 30-4
[4] He D P 2013 *Oil Chemistry* (Beijing: Chemical Industry Press) pp 191-2
[5] Narayana T, Kaimal B, Vail S R, et al 2002 Origin of problems encountered in rice bran oil processing *European J. of Lipid Sci. & Technol.* 104 203-11
[6] Zhao G H, Niu X Y, Jiang W, et al 2014 Refining and degumming mechanism analysis of jatropha crude oil *Cereals & Oils Processing* 2 47-9,52
[7] Jiang X F, Xia Y, Jin Q Z, et al 2013 Optimization of acid-assisted degumming of crude rapeseed oil *China Oils & Fats* 38(6) 4-8
[8] Wu Y J, Zhang X, Song G H, et al 2014 Optimization of acid degumming process of cold pressed Sesame oil *Sci. & Technol. of Food Ind.* 17 205-8
[9] GB/T 5537-2008 Inspection of grain and oils-Determination of phosphatide content
[10] GB/T 5530-2005 Animal and vegetable fats and oils-Determination of acid value and acidity
[11] GB/T 5534-2008 Animal and vegetable fats and oils-Determination of saponification value
[12] GB/T 5532-2008 Animal and vegetable fats and oils-Determination of Iodine Value