Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S217-S221

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19051

Preparation of Gallic Acid Esters and Their Antioxidant Properties for Biodiesel

FASHE LI[1,2], MING LI[3,*], GUIRONG BAO[1,2], HUA WANG[1,2], YIZHE LI[1], WEI DU[1] and XIUFENG LI[1]

[1]Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, P.R. China
[2]Engineering Research Center of Metallurgical Energy Conservation and Emission Reduction, Ministry of Education, Kunming University of Science and Technology, Kunming 650093, P.R. China
[3]Department of Engineering, Oxbridge College, Kunming University of Science and Technology, Kunming 650106, P.R. China

*Corresponding author: E-mail: lm_paper@qq.com

Published online: 24 December 2014; AJC-16476

This study investigates the use of the *p*-toluene sulphonic acid as catalyst and a microwave heating system for synthesizing gallic acid esters from gallic acid and acohols, which include methyl-3,4,5-trihydroxybenzoate, ethyl gallate, propyl gallate, isopropyl gallate, *n*-butyl gallate, isobutyl gallate and *tert*butyl gallate. The gallic acid esters are analyzed by the FTIR. The antioxidant effect to biodiesel and the raw oils are studied with the dosage of 1000 ppm each and it shows better oxidation stability. With the increase of the antioxidants isopropyl gallate and isobutyl gallate, the induction period of the biodiesel are longer. When 250 ppm of isopropyl gallate and 600 ppm of isobutyl gallate are added, the oxidation stability of biodiesel can meet Chinese national standards and European standards.

Keywords: Biodiesel, Antioxidants, Antioxidant properties, Induction period.

INTRODUCTION

The main components of biodiesel are long-chain fatty acids, and polyunsaturated fatty acids contents which contain carbon-carbon double bonds have also surpassed a half of them[1-4]. The polyunsaturated fatty acids are oxidized easily during the stored procedure for the environments of oxygen, light or metal ions, that will produce many peroxides. Because of the instability of the peroxides, they breaks down into many secondary oxidation product, such as water, alcohol, organic acids, polymers, precipitation and so on. These products will cause evil odors, filtration difficulty and layering of biodiesel, even cause problems of motor corrosion, oil line clogging or output power fluctuation of motor. So biodiesel oxidation not only affect the quality of the biodiesel, but also affect the operation of the vehicle system or even reduce the service life of them.

Several papers have reported this problem[4-8]. Bouaid[9] has studied the change of the biodiesel on acids ester, peroxides, viscosity, oxidation product and iodine value during 40 months. At last, they proposed the store time of biodiesel might be longer at the condition of without light, sealing and water-proofing. Park *et al.*[10] and Sarin *et al.*[11] advocated to improve the oxidation stability by mixing different kinds of biodiesel. Warwel *et al.*[12] indicated that the unsaturated fatty acid methyl ester specially linolenic acid which has three double bonds influenced the oxidation stability of biodiesel. Graz[13] studied the effects of several natural antioxidant to biodiesel oxidation stability, such as α-VE, γ-VE, δ-VE, carotenoid, retinoic acid and astaxanthin. Mittelbach and Schober[14-16] first proposed that propyl gallate, TBHQ, BHA, BHT can improve the oxidation stability of bio-diesel. The aim of this work is to synthesize seven new gallate

EXPERIMENTAL

Ultra pure water (self-prepared), *Jatropha curcas. L* seed oil and *Jatropha curcas. L* seed biodiesel oil (self-prepared), methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, gallic acid, *p*-toluenesulfonic acid, sulfuric acid, pyridine, acetone, absolute ethyl alcohol, petroleum ether and *n*-heptane are used as such.

Apparatus: A distilled water generator, FA1604 electronic balance, FT-IR spectrometer (FTS-40), ultrasonic cleaner, oxidation stability determinator of biodiesel (Rancimat873), ultrahigh performance liquid chromato-graphy (Acquity-UPLC^{TM}).

The gallic acid and alcohol were placed in a 500 mL three-necked flask fitted with a reflux condenser, a thermometer and a heater in an ultrasound machined. Put the catalyst into the solution and heat it to the desired temperature for a certain time through ultrasonic auxiliary. Fig. 1 shows the experimental equipment. Distill unreacted alcohol from the solution, then dissolve in deionized water and cool in the refrigerator. After that crystalline substance will be separated from the solution. Filter the crystalline substance from the solution and vacuum dry about 24 h. Then the purified product are obtained. The chemical reaction equation is showed in Fig. 2.

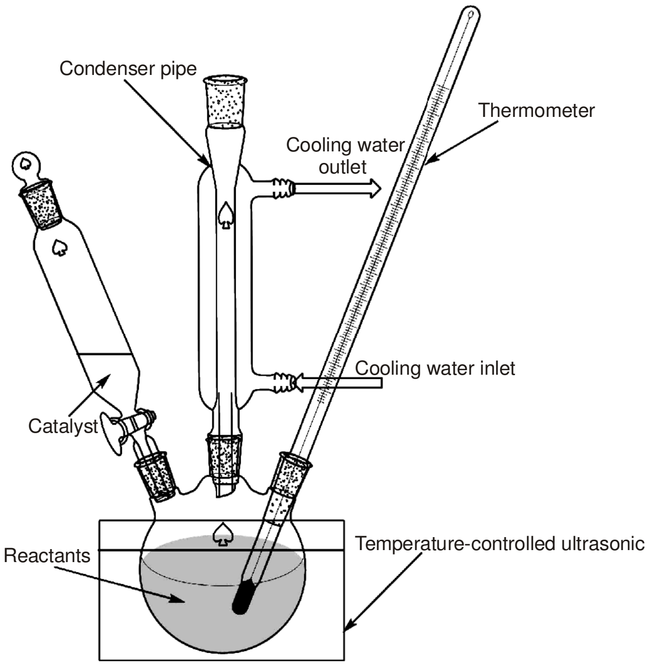

Fig. 1. Experimental installation diagram of preparation to biodiesel antioxidant

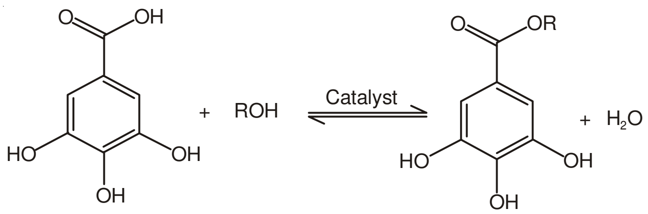

Fig. 2. Esterification reaction between gallic acid and alcohols

The test use Rancimat method to determine the oxidation stability by EN 14112-2003 that the test (accelerated oxidation test) of oxidation stability for grease, oil derivatives and fatty acid methyl ester. As this method, the air that heated to a definite temperature pass though the self prepared antioxidant and the unstable secondary oxidation products will be brought in another glass bottle containing ultrapure water, which will make the electrical conductivity of ultrapure water changed. Use the electrode to test the changes of electrical conductivity in ultrapure water and make a diagram by electrical conductivity and time.

The curve of electrical conductivity changes with time obtained. The induction period time is the second derivative of this curve. The induction period time refers to the time of electrical conductivity mutations in water which could be obtained by calculating the slope of the curve. For the sample of biodiesel, the induction time is the long the better. So, this method is taken to evaluate the oxidation stability of biodiesel sample. The principle and procedure are shown in Fig. 3. Fig. 4 shows the changing curve of electrical conductivity with time and its second derivative curve.

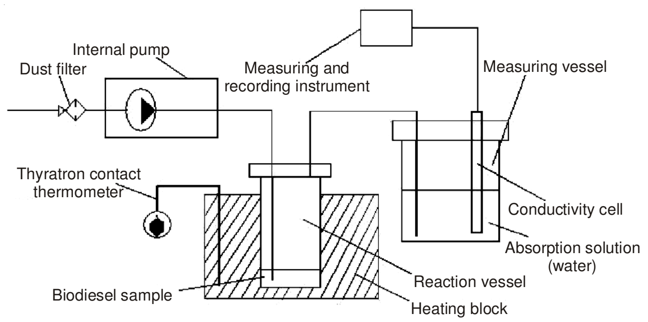

Fig. 3. Flow diagram of oxidation stability test principle

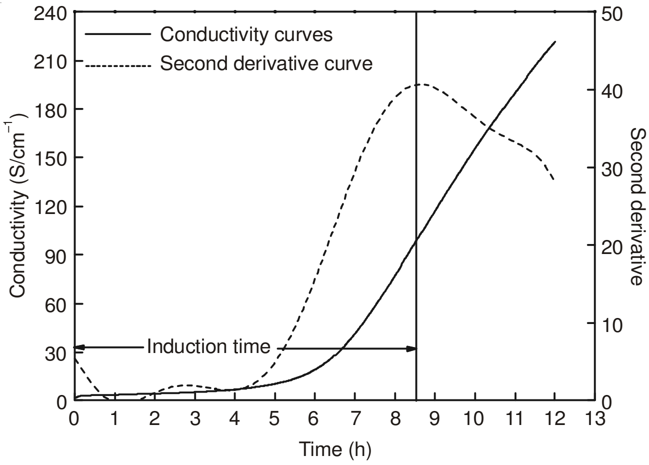

Fig. 4. Curve graph of oxidation stability to test sample

RESULTS AND DISCUSSION

Analysis of self-made antioxidant properties: The esterification of gallic acid and methyl alcohol, ethyl alcohol or *n*-butyl alcohol uses *p*-toluenesulfonic acid as catalyst. With the assistance of ultrasonic, the reaction temperature is around 70 °C the time of reaction is 3-6 h, yield could reach 92 %. When use ionic liquid as catalyst, with the assistance of ultrasonic, the reaction temperature is around 85 °C, the time of reaction is 4-7 h, the yield could reach 95 %. For the reason that the reaction of gallic acid and isopropyl alcohol, isobutyl alcohol and *tert*butyl alcohol is difficult, that we use different catalysts. It shows that use of *p*-toluenesulfonic acid as catalyst and react for 6 h, the yield is only 50 %. By contrast, if use pyridine bisulfate ionic liquid as catalyst, fast reaction rate and the conversion rate of esterification can reach 95 %.

The infrared spectra of isopropylgallate is shown in Fig. 5. The absorption peak of 3498 and 3280 cm^{-1} are the stretching vibrational absorption peak of phenolic hydroxyl groups O-H. The absorption peak of 1541 and 1467 cm^{-1} is benzene ring stretching vibrational absorption peak.

The absorption peak of 1667 cm^{-1} is the stretching vibrational absorption peak of carboxyl C=O. The absorption peak 1387 cm^{-1} is the stretching vibrational absorption peak of C-O-C. The absorption peak of 1321 cm^{-1} is the stretching vibrational absorption peak of -$CH(CH_3)_2$. All of those data match with the structure of isopropylgallate. The infrared spectra diagrams of other gallic acid esters are shown in Fig. 6.

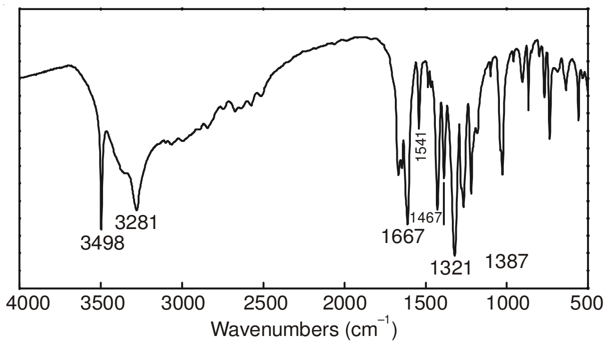

Fig. 5. FTIR spectrum of isopropyl gallate

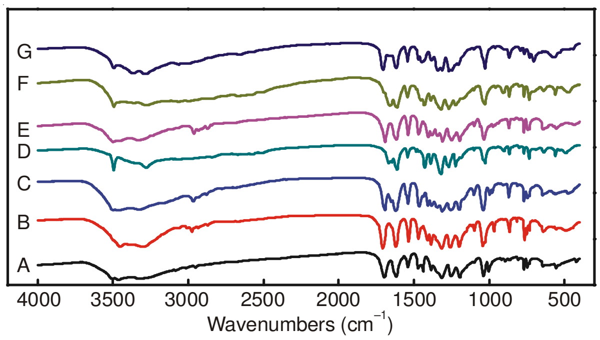

Fig. 6. FTIR spectrum of gallate organic ester compound; (A: 3,4,5-Trihydroxybenzoate B: Ethyl gallate C: Propyl gallate D: Isopropyl gallate E: *n*-Butyl gallate F: Isobutyl gallate G: *tert*-butyl gallate)

Antioxidant properties for biodiesel feedstock of self-made antioxidant: The seven self-made antioxidants, methyl-3,4,5-trihydroxybenzoate (MT), ethyl gallate (EG), propyl gallate (PG), isopropyl gallate (iPG), *n*-butyl gallate (BG), isobutyl gallate (iBG) and *tert*butyl gallate (tBG), are added 1000 ppm to *Jatropha curcas. L* seed oil or rapeseed oil separately. The induction period time are tested, respectively in the same conditions (Figs. 7 and 8). Self-made antioxidants have good effect on *Jatropha curcas. L* seed oil and rapeseed oil. Among these self-made antioxidants, the antioxidant effect of isopropyl gallate, isobutyl gallate, *tert*butyl gallate, propyl gallate and *n*-butyl gallate to *Jatropha curcas. L* seed oil and rapeseed oil are better than that of methyl-3,4,5-trihydroxybenzoate and ethyl gallate.

This also indicates that the antioxidant effect of these seven antioxidants to *Jatropha curcas. L* seed oil are better than that to rape seed oil by analyzing Figs. 7 and 8. Because the main ingredient of *Jatropha curcas. L* seed oil are unsaturated fatty acids which contained double bonds and triple bonds. *Jatropha curcas. L* seed oil oxidized easily during storage which reduce the performance of the oil. It is good for *Jatropha curcas. L* seed oil storage when these seven antioxidants are used and the storage time will be extended greatly. But it needs the help of ultrasonic to dissolve methyl gallate or propyl gallate in *Jatropha curcas. L* seed oil completely for the bad solubility property of them. Other antioxidants can be dissolved in the oil completely after stir for the great solubility of them.

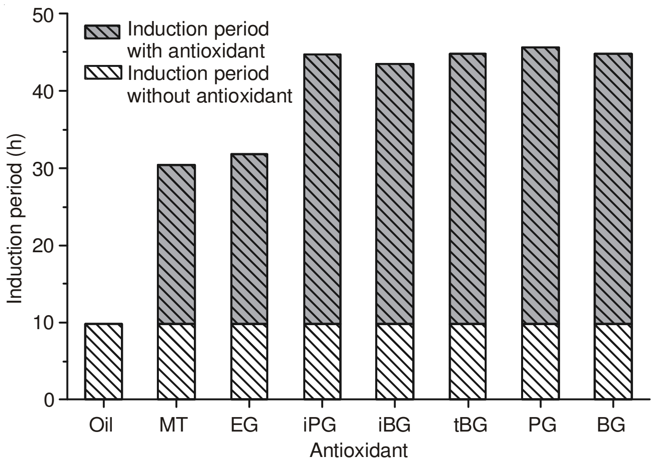

Fig. 7. Effect of preparative antioxidant to *Jatropha curcas. L* seed oil oxidation stability

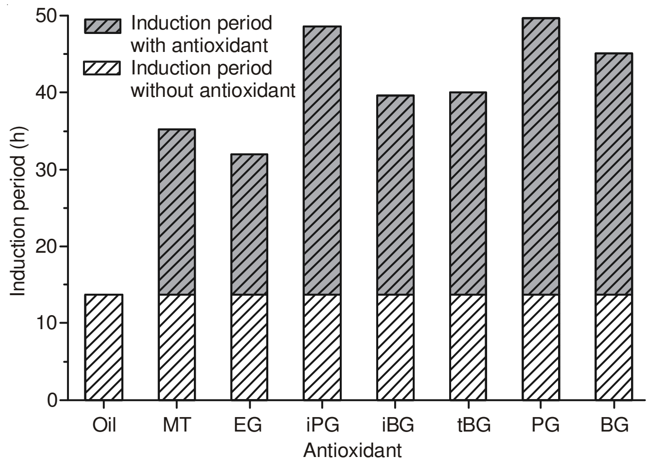

Fig. 8. Effect of preparative antioxidant to rape seed oil oxidation stability

Antioxidant properties for biodiesel of self-made antioxidants: Using *Jatropha curcas. L* seed oil biodiesel as sample which is prepared by using circulating gaseous esterification-transesterification-methanol steam distillative purification process[17,18], then add seven self-made antioxidants to the sample. For comparison purposes, mix up *Jatropha curcas. L* seed oil biodiesel which is not purified by methanol steam distillation with seven kinds of antioxidants. Their addictive amount of antioxidants in the two groups experiments both are 1000 ppm. The induction period time of biodiesel was tested under the same conditions and on this basis the influence of oxidation stability was studied when the seven self made antioxidants were added to the *Jatropha curcas. L* seed oil biodiesel. Figs. 9 and 10 are the bar charts which show the effect of preparative antioxidants to *Jatropha curcas. L* seed oil biodiesel. From the figures, these seven antioxidants play a good effect to the oxidation stability of the purified *Jatropha curcas. L* seed oil biodiesel and it makes the induction period time become longer. Because the main ingredient of *Jatropha curcas. L* seed oil biodiesel is unsaturated fatty acid methyl ester which contained one or more double bonds, its properties is unstable. It is so vulnerable to be oxidized that its oxidation stability couldn't reach national standard. When adding quantity of these seven kinds of antioxidants are low (1000 ppm), the oxidation stability of *Jatropha curcas. L* seed oil biodiesel approach to biodiesel national standard only when isobutyl gallate is used. And the others could meet national standard of biodisesel.

Performance comparison between self-made and purchase antioxidant: Fig. 11 shows the comparison of the effect to oxidation stability between self-made antioxidants and purchased ones. The conclusion could be obtained from the Fig. 11 that the antioxidant effect of self-made antioxidants is better than the others. It is almost the same on antioxidant effect when use purchased propyl gallate or self-made methyl-3,4,5-trihydroxybenzoate. However, antioxidant effect of purchased methyl-3,4,5-trihydroxybenzoate to *Jatropha curcas. L* seed oil biodiesel is different greatly from self-made one. The antioxidant effect of self-made methyl-3,4,5-trihydroxybenzoate is much better than purchased one. When the adding amount both are 1000 ppm, the oxidation stability of purchased methyl-3,4,5-trihydroxybenzoate to *Jatropha curcas. L* seed oil biodiesel couldn't achieve national standard of biodesel 6 h, while the induction time of *Jatropha curcas. L* seed oil biodiesel could reach 9.61 h when use self-made methyl-3,4,5-trihydroxybenzoate. The reason perhaps is that the purity of self-made methyl-3,4,5-trihyd-roxybenzoate is higher than purchased methyl-3,4,5-trihydroxybenzoate. The oxidation stability of biodiesel can't achieve the national standard of biodiesel for several others purchased antioxidants when the adding quantity are 1000 ppm. To qualify, we would have to increase the adding quantity of these purchased antioxidants. But at the same time, it would increases cost. When all of these problems are considered together, it is the best choice to use self-made gallic acid esters as antioxidants for *Jatropha curcas. L* seed oil.

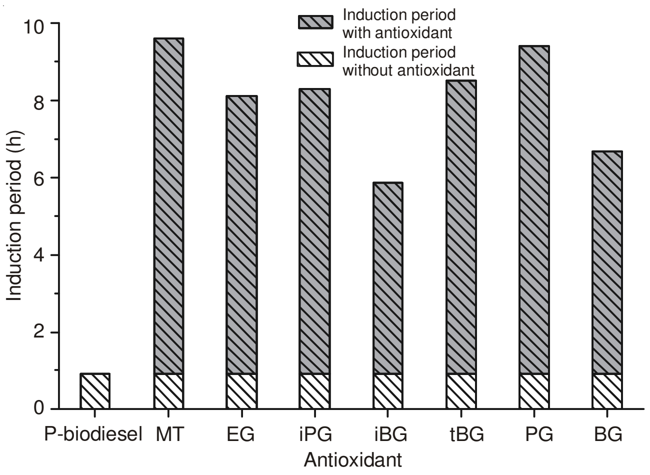

Fig. 9. Effect of preparative antioxidant to *Jatropha curcas. L* seed oil biodiesel oxidation stability (refined)

Effect of dosage on biodiesel oxidation stability of self-made antioxidant: Select isopropyl gallate, isopropyl gallate and isobutyl gallate, in-butyl gallate, among the c7 self-made antioxidants to study the effect of antioxidants on adding quantity to oxidation stability of crude *Jatropha curcas. L* seed oil biodiesel. From the Fig. 12, the induction period time become longer with the adding quantity of antioxidant increasing and the growth amplitude is larger. In that case any further increase in the adding quantity will have a little effect and

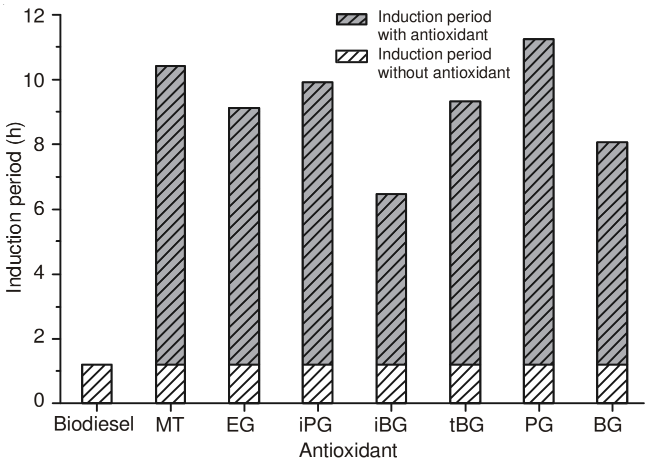

Fig. 10. Effect of preparative antioxidant to *Jatropha curcas. L* seed oil biodiesel oxidation stability (rough-wrought)

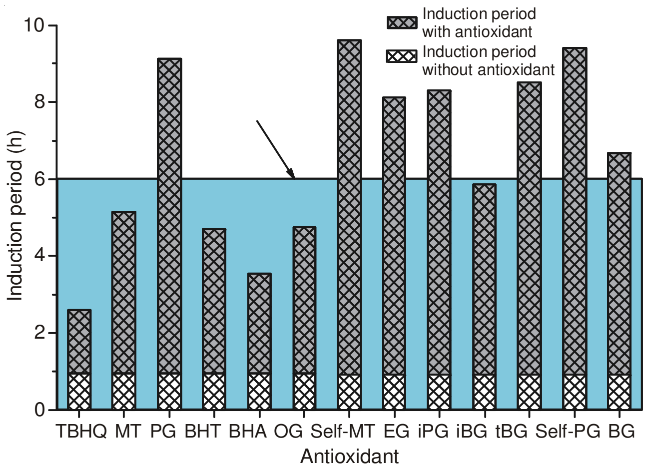

Fig. 11. Effect of various antioxidant to *Jatropha curcas. L* seed oil biodiesel oxidation stability (refined)

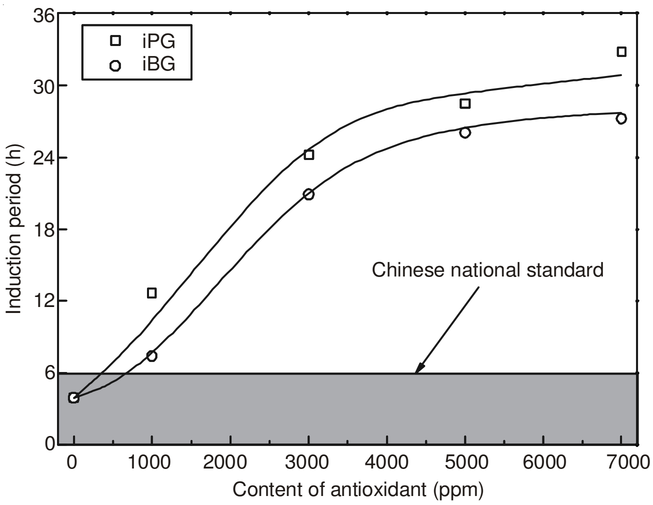

Fig. 12. Effect of antioxidant content to *Jatropha curcas. L* seed oil biodiesel oxidation stability

reaction tends to become steady. And out of this information, the oxidation stability of crude *Jatropha curcas. L* seed oil biodiesel can achieve national standard of biodiesel with a little quantity of antioxidants. When the adding quantity of isopropyl gallate is 250 ppm or the adding quantity of isobutyl gallate is 600 ppm, the oxidation stability of crude *Jatropha curcas. L* seed oil biodiesel can achieve both Chinese national standard and European standard of biodiesel.

Conclutions

• Using *p*-toluene sulphonic acid and sulfuric acid ionic liquid as catalyst, seven different kinds of antioxidants of gallic acid esters included methyl-3,4,5-trihydroxybenzoate, ethyl gallate, propyl gallate, isopropyl gallate, *n*-butyl gallate isobutyl gallate and *tert*butyl gallate were prepared. The gallic acid esters are analyzed by the FTIR and match the structure.

• The antioxidant effect of raw oil biodiesel are studied when seven self-made antioxidants are used. The induction period time of for *Jatropha curcas. L* seed oil and rape seed oil are obviously much longer when the adding quantity of antioxidants is 1000 ppm.

• The antioxidant effect to *Jatropha curcas. L* seed oil biodiesel are studied by using seven self made antioxidants. Only the oxidation stability of isobutyl gallate can't achieve our national standard of biodiesel when the adding quantity is 1000 ppm. In comparison with purchased antioxidants, antioxidant effect of *Jatropha curcas. L* seed oil biodiesel with self-made antioxidants is much better than with purchased ones.

• The effect of adding quantity of isopropyl gallate and isobutyl gallate to oxidation stability of biodiesel are studied. The induction period time become longer and the growth amplitude is larger when increase the adding quantity of antioxidant. When the adding quantity of isopropyl gallate is 250 ppm or the adding quantity of isobutyl gallate is 600 ppm, the oxidation stability of crude *Jatropha curcas. L* seed oil biodiesel can achieve both Chinese national standard of biodiesel and European standard of biodiesel.

ACKNOWLEDGEMENTS

Sponsored by the Doctoral Fund of Ministry of Education of China Project management (KKQX 201352004) and Natural Science Fund Project in Yunnan province (KKSY201252021); conducted at the Engineering Research Center of Metallurgical Energy Conservation & Emission Reduction at Kunming University of Science and Technology, Kunming, Yunnan, China.

REFERENCES

1. M. Balat and H. Balat, *Appl. Energy*, **87**, 1815 (2010).
2. M.B. Dantas, A.R. Albuquerque, A.K. Barros, M.G. Rodrigues Filho, N.R. Antoniosi Filho, F.S.M. Sinfronio, R. Rosenhaim, L.E.B. Soledadef, I.M.G. Santosa and A.G. Souza, *Fuel*, **90**, 773 (2011).
3. M.J. Ramos, C.M. Fernández, A. Casas, L. Rodríguez and Á. Pérez, *Bioresour. Technol*., **100**, 261 (2009).
4. F. Li, G. Bao and H. Wang, *China Oils and Fats*, **34**, 1 (2009).
5. G. Knothe, *Fuel Process. Technol*., **88**, 669 (2007).
6. C.-Y. Lin and C.-C. Chiu, *Energy Convers. Manage*., **51**, 1464 (2010).
7. G. Karavalakis, D. Hilari, L. Givalou, D. Karonis and S. Stournas, *Energy*, **36**, 369 (2011).
8. V.M.L. dos Santos, J.A.B. da Silva, L. Stragevitch and R.L. Longo, *Fuel*, **90**, 811 (2011).
9. A. Bouaid, M. Martinez and J. Aracil, *Fuel*, **86**, 2596 (2007).
10. J.-Y. Park, D.-K. Kim, J.-P. Lee, S.-C. Park, Y.-J. Kim and J.-S. Lee, *Bioresour. Technol*., **99**, 1196 (2008).
11. A. Sarin, R. Arora, N.P. Singh, M. Sharma and R.K. Malhotra, *Energy*, **34**, 1271 (2009).
12. S. Warwel, F. Brüse, C. Demes, M. Kunz and M.R. Klaas, *Chemosphere*, **43**, 39 (2001).
13. Stability of Biodiesel Used as a Fuel for Diesel Engines and Heating Systems, Presented at BIOSTAB Project Results, Graz, Austria, July 3 (2003).
14. S. Schober and M. Mittelbach, *Eur. J. Lipid Sci. Technol*., **106**, 382 (2004).
15. M. Mittelbach, M. Wörgetter, J. Pernkopf and H. Junek, *Energy in Agric.*, **2**, 369 (1983).
16. L. Akselrod, H.J. Byrne, C. Thomsen, A. Mittelbach and S. Roth, *Chem. Phys. Lett*., **212**, 384 (1993).
17. Y. Su, W. Zhang, Z. Ge and W. Shi, *J. Kunming Univ. Sci. Technol*., **31**, 87 (2006).
18. D. Wang, Y. Su, H. Wang and G. Bao, *China Oils and Fats*, **34**, 46 (2009).