Effects of Synthetic Antioxidants and Garlic Extracts on the Stability of Crude Jatropha Oil

Tsair-Wang Chung, Chen-Ju Chen, Shun Gao, and Chung-Ping Chou

***Abstract*—**Effects of propyl gallate (PG), butylated hydroxyanisole (BHA) and garlic extract on the stability of crude Jatropha oil (CJO) were investigated at 25°C and 45°C for 12 months. Parameters of CJO were measured every three months, including acid value, free fatty acid (FFA), rancimat induction period (RIP) and water content, etc. Our results suggested that acid values, FFA and water contents of CJO increase at different storage time and temperatures as well as under the addition of antioxidant conditions except for some special conditions. RIP value decreased gradually with the prolonging storage time under no addition of antioxidant condition. However, these values increased significantly under the addition of different antioxidant condition compared to the control, and these increments decreased gradually with the prolonging storage time compared to the control. These results indicated that the oxidation stability of CJO show no significant difference between synthetic antioxidants and garlic extract at different temperatures during the long-term storage, and are significantly higher than those of no addition.

***Keywords*—**Jatropha oil, oxidant stability, antioxidant, garlic extraction.

I. Introduction

JATROPHA curcas, a multipurpose, drought-tolerant, fast-growing, renewable bio-energy plant belonging to Euphorbiaceae family, which has attracted the attention of investors and policy-makers worldwide for the purpose of producing bio-fuel in recent years. Its seed typically contains 30-40% oil, which has properties highly suited to making bio-diesel. Its by-products may potentially be used as fertilizer, livestock feed, or as a biogas feedstock. [1] Unlike other major bio-fuel crops, J. curcas is not a food crop and its oil is non-edible oil for its phorbol ester and other toxins, but can serve as bio-fuel in adapted diesel. [2] Plant oil consists of phospholipids, free fatty acids, pigments, sterols, carbohydrates and proteins, etc, and these substances and unsaturated fatty acids can be oxidized or degradated during the storage conditions. Thus, the color and stability of oils would be changed, and quality and consistency of oil reduce significantly. [2-3]

Oxidation mechanism of plant oils is a complex series of reactions, and the process is further complicated by different conditions, such as temperature, pressure and oxygen availability, etc. Oxidation reaction starts to take place immediately after oil extraction. Although it can not be stopped, there are some methods that may be taken to slow down this process. Addition of antioxidants in the oils may help to slow oxidation or degradation processes and increase their oxidation stability. [3] Synthetic antioxidants, like propyl gallate (PG) and butylated hydroxyanisole (BHA), are generally used to retard oxidation reaction and improve the oxidation stability of plant oil during the storage process. [4] Earlier reports have suggested that the addition of PG and BHA in sunflower and soybean oil may maintain a better stability and quality than those of no addition of antioxidants during the storage process. [5] Recently, there is a highly desirable for effective antioxidants from natural sources as alternatives to replace the synthetic antioxidants. It was reported that the extracts from different plant species possess varying degrees of antioxidant activities. Some reports have suggested that some extracts from plant species have different enhancement effects on the oxidant stability of different plant oils. [6] These findings suggested that the effects of different types of synthetic and natural antioxidants in slowing down the oxidation process of plant oils are available.

Although there is a series of studies about the effects of different synthetic and natural antioxidants on the storage stability of plant oils, little information is available concerning the effects of synthetic and natural antioxidants on storage stability of Jatropha oil during the storage period of 12 months. In this study, the storage stability of crude Jatropha oil was investigated over a storage time of 12 months under the addition of antioxidants and different storage temperatures. Several parameters of oil properties, such as acid value, free fatty acid, and rancimat induction period were analyzed from samples from each storage conditions. The present results will lead to a better understanding of the effects of storage conditions and antioxidants on the stability of crude Jatropha oil.

II. Material and Methods

Butylated hydroxyanisole (BHA) and propyl gallate (PG) were purchased from TCI. Garlic was obtained from local supermarket. All reagents and solvents used were of analytical

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reagent grade. Mature jatropha seed was purchased from Indonesia. Jatropha oil was obtained by mechanical pressing. Seeds were roasted about the temperatures ranging from 70 to 80°C. After pressing, the impurities and gum particles of the oil was removed using filtration and the oil was stored for further use.

Garlic extract was prepared by the following method. In brief, garlic was washed and then oven-dried at 60°C for approximately 24 h. The dried materials were ground and extracted with methanol (m/v, 1/10) in a shaker for 24 h at room temperature. Extract was filtered through Whatman No. 4 filter paper. The residue was extracted twice by adding methanol each time, as described above. These extracts were combined and evaporated in a rotary evaporation below 40°C for further experiments. In addition, the yield, antioxidant activity and thermal stability of garlic extract were calculated and measured according to the method in the literature. [7]

Oil samples were transferred into brown glass bottle with lips (100 ml), and they were randomly divided into ten groups, each consisting of 3 bottles with 70 ml oil samples. One group without addition of antioxidants at 25°C was served as control. The other four groups were added by 200 ppm PG, 200 ppm BHA, 1600ppm and 2400ppm garlic extract in the oils at 25°C before the experiments, respectively. Similarly, remaining five groups including no antioxidants, PG, BHA and garlic extract were placed at 45°C for the accelerated tests of long-term storage. The oil samples were take out every three months and used as determining acid value, free fatty acid, rancimat induction period and water content of oil.

Acid value was measured by the method of AOCS (1999). Acid values were expressed as microgram KOH per gram oil sample (mg KOH/g). Free fatty acid (FFA) values were determined from acid values according to the method of AOCS (1997). FFA values were expressed as percentage (%). Oxidative stability is quantified by the rancimat induction period of Jatropha oil. The measurements of rancimat induction period were carried out on a Metrohm 873 Rancimat (Brinkmann Instruments, Westbury, NY) according the method described by introduction. RIP were expressed as hour. Water content was measured using a Karl Fischer coulometer (831 KF coulometer, Metrohm, Herisau, Switzerland) according to the method described by introduction. Reported data is the mean of three replicates. Statistical analysis was conducted in a randomized complete factorial model, and Tukey test ($P < 0.05$) was applied to treatments time average values.

III. Results

As shown in Fig.1, acid values increased gradually with the prolonging storage time up to 12 month at 25°C compared to the control, and the highest values increased by 94.3%, 82.9%, 83.8%, 78.6% and 55.7% with no addition, 200 ppm PG, 200 ppm BHA, 1600 ppm garlic extract and 2400 ppm garlic extract, respectively. Similarly, acid values increased significantly with no addition, 200 ppm PG, 200 ppm BHA, 1600 ppm garlic extract and 2400 ppm garlic extract at different storage times compared to the control, and these highest increments reached increases of 145.7%, 130%, 139.5%, 82.9% and 67.1%, respectively (Fig.2).

FFA values increased by 22.5%, 41.4%, 51.4% and 93.7% for 3, 6, 9 and 12 months at 25°C, respectively. Under the addition of 200 ppm PG, 200 ppm BHA, 1600 ppm garlic extract and 2400 ppm garlic extract, these increments of FFA values decreased significantly at different storage times compared to those of no addition, and the highest increased values are 82%, 82.9%, 77.5% and 55% at 12 months, respectively (Fig.3). As shown in Fig.4, FFA values increased by 41.4%, 46.8%, 64.9% and 145% for 3, 6, 9 and 12 months at 45°C compared to the control, respectively. Increments of FFA value decreased significantly under the addition of antioxidants and extract compared to those of no addition, and the highest levels increased by 128.8%, 138.7%, 82% and 66.7% when CJO was stored for 12 months under 200ppm PG, 200ppm BHA, 1600 ppm garlic extract and 2400 ppm garlic extract, respectively. However, FFA values decreased significantly in the beginning when 200ppm PG, BHA and garlic extract were added at 45°C compared to the control.

As shown in Fig.5, RIP decreased gradually with the prolonging storage time up to 12 months at 25°C, the largest decrease being 26.3% (6.67 h) compared to the control. Under the addition of 200 ppm BHA, these values kept stable during the long-term storage at 25°C except for that of 0 month compared to the control. However, these values showed significant increases for different storage times at 25°C when 200 mM PG, 1600 ppm and 2400 ppm garlic extract were added, and the lowest increments reached 43.2%, 15.2% and 17.7% for 12 months compared to the control, respectively. Under the storage of 45°C condition, these values decreased gradually with the prolonging storage times up to 12 month with no addition, PG, BHA and garlic extract compared to the control. However, the values with the addition of PG, BHA and garlic extract at different storage times are higher than those of no addition.(Fig.6)

Under no additives condition, water contents rose significantly up to 12 months at 25°C compared to the control, and the highest levels reached about 11.28 times higher than that of the control. When 200 ppm PG, 200 ppm BHA, 1600 and 2400 ppm garlic extract were added before experiments, the largest levels of water contents for 12 months represented 10.42, 10.45, 10.34 and 10.11 times higher than that of the control, respectively (Fig.7). As shown in Fig.8, water contents increased progressively as the storage process up to 12 months under no addition and different antioxidants compared to the control. The highest values with no addition, 200 ppm PG, 200 ppm BHA, 1600 and 2400 ppm garlic extract were 11.5, 10.8, 11.7, 11.3 and 10.6 times greater than that of the control,

respectively.

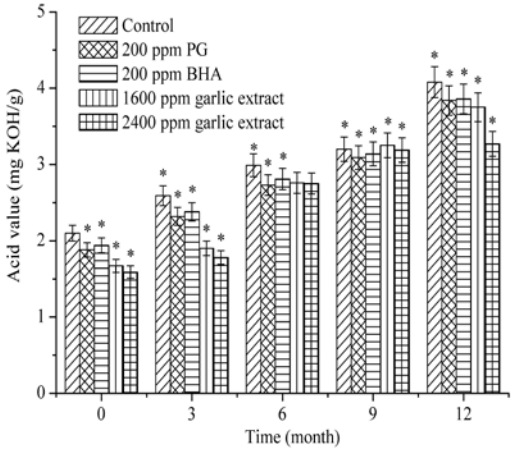

Fig. 1 Effects of PG, BHA and garlic extract on acid value of crude Jatropha oil for 12 months at 25°C

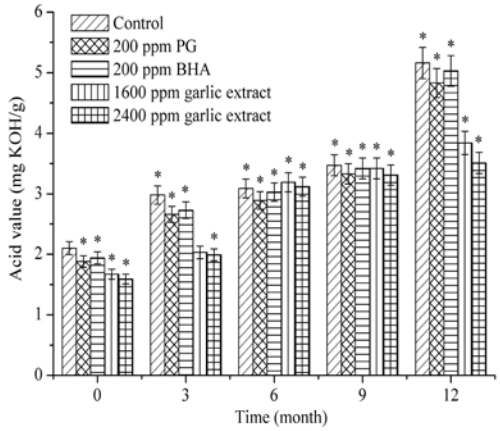

Fig. 2 Effects of PG, BHA and garlic extract on acid value of crude Jatropha oil for 12 months at 45°C

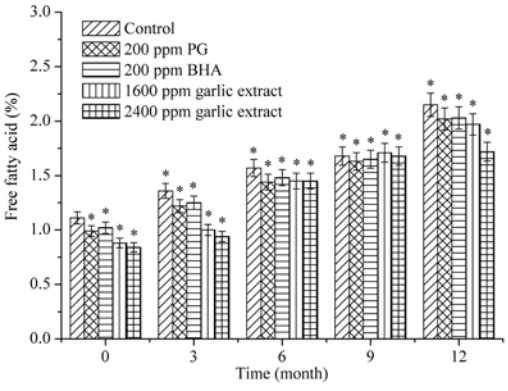

Fig. 3 Effects of synthetic antioxidants and garlic extract on free fatty acid value of crude Jatropha oil for 12 months at 25°C

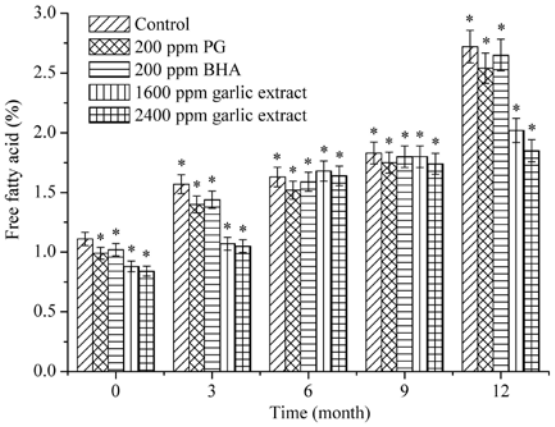

Fig. 4 Effects of synthetic antioxidants and garlic extract on free fatty acid value of crude Jatropha oil for 12 months at 45°C

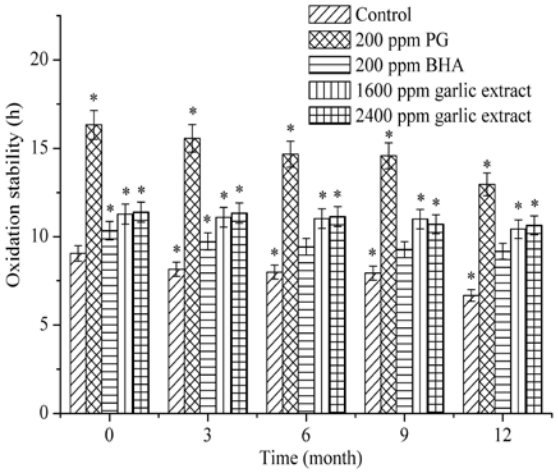

Fig. 5 Effects of synthetic antioxidants and garlic extract on rancimat induction period of crude Jatropha oil for 12 months at 25°C

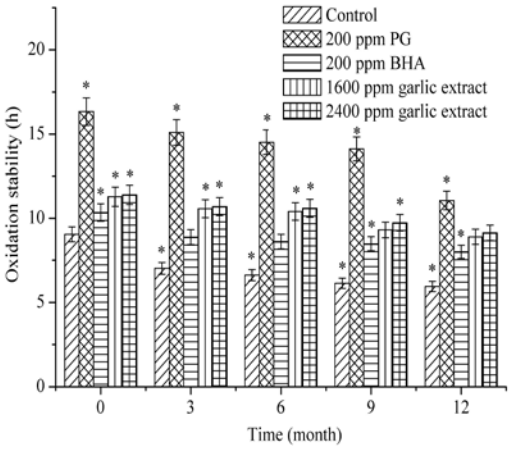

Fig. 6 Effects of synthetic antioxidants and garlic extract on rancimat induction period of crude Jatropha oil for 12 months at 45°C

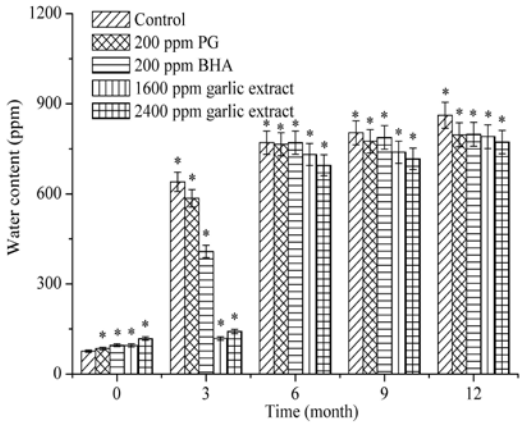

Fig. 7 Effects of synthetic antioxidants and garlic extract on water content of crude Jatropha oil for 12 months at 25°C

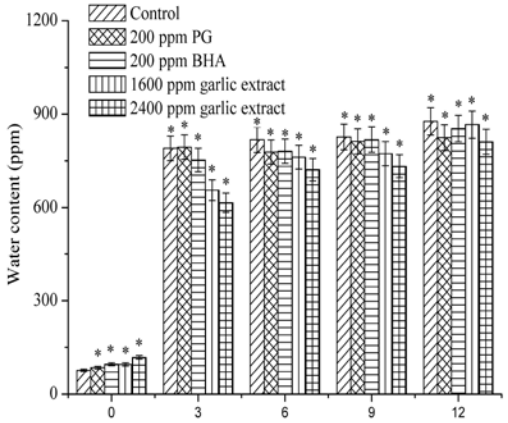

Fig. 8 Effects of synthetic antioxidants and garlic extract on water content of crude Jatropha oil for 12 months at 45°C

IV. Discussions

Plant oils are partially oxidized when contacted with oxygen at elevated temperatures during the storage period. Oxidation process produces rancid odours, unpleasant flavours and discoloration, and decreases the quality and stability of oils. Addition of antioxidant is a simple method that delay or prevent lipid oxidation, preserve the quality and extend the shelf-life of plant oils. Several effective antioxidants have been used in the storage and stability of the vegetable oil and/or biodiesel. These antioxidants, while exhibiting good antioxidant properties, are burdened by economic and oil quality problems. Thus, these findings suggested that the addition of antioxidants may be involved in improving the oxidant stability of plant oil and/or bio-diesel, and that is economical and easy to produce. In the present study, storage stability of crude Jatropha oil with the different antioxidants was investigated over a storage time of 12-months under 25 °C and 45 °C. The aim of this study was to investigate the effects of the addition of PG, BHA and garlic extract in the protection of crude Jatropha oil against lipid oxidation.

Acid value is an important indicator of oil quality. However, the acid value of oil must not be too high, as this denotes an excessively high content of free fatty acids, which causes the oil to turn sour (AOCS, 1999). In the present study, acid values increased significantly with the prolonging storage time under different antioxidant, storage time and temperature conditions, except for those of the addition of garlic extract at 3 months. These values with the addition of PG and BHA are significant lower than those of the controls under different conditions, but they are higher than those of under the addition of garlic extract condition. These changes are significantly observed between 25℃ and 45℃ during the long-term storage (Figs. 1 & 2). These results suggested that PG and BHA may play important roles in the oxidation stability and quality of Jatropha oil, and garlic extract show the more effective antioxidant capacity compared to those of PG and BHA. FFA content in the oils is also an important quality parameter during the storage. In the present study, the determination of fatty acid value was carried out by colorimetric method (AOCS, 1997). Our results suggested that the significantly increased FFA values in the oils are observed at different time, temperatures and antioxidants during the storage except for those of at 3 months under the addition of garlic extract condition. In addition, the increased values in the oils with the addition of garlic extract are lower than those of under the addition of PG and BHA condition as well as the control. FFA contents may affect the increase of acid values in the oils, and the higher FFA values reflect the increased acidity levels.

RIP is well correlated with oxidative stability of oils and diesel. Higher RIP value suggests that the oil or diesel is less susceptible towards oxidation reaction during the storage. The value of a minimum RIP is 6 h based on the european standard for biodiesel (EN 14214) and pure plant oil (DIN51605). In the present study, RIP of crude Jatropha oil is 9.05, which is significant higher than that of the minimum RIP. RIP values decreased gradually with the prolonging storage time under no addition of antioxidants compared to the control, and the lowest values is 5.96 h. However, these values of oils with the addition of PG, BHA and garlic extract increased significantly during the long-term storage compared to those of under no addition of antioxidant (Figs. 5 & 6). In addition, the changes in RIP values of the oil are correlated to the significant increases in acid value, free fatty acid values and water contents under different temperatures during the storage. Our results suggested that the

RIP values in the all oils samples are higher than the standard value (6 h) under the addition PG, BHA and garlic extract condition. Varieties of RIP values in some vegetable oils with the addition of different synthetic antioxidants and natural extracts were observed during different storage condition, and differential protect roles of antioxidants were found. Our findings also further support the facts that synthetic antioxidants and natural extracts play important roles in maintaining the relative high RIP values of Jatropha oil.

During the bio-diesel production, the higher water content in the oils has negative effects on the transesterification reaction, such as soap formation, catalyst consume and reduced catalytic activity, which cause a decreased yield. Thus, water content in the oils is usually kept below 0.1 wt% or less. Our results suggested that the value of water content of the fresh crude Jatropha oil is about 76.4 ppm, but the values increased significantly with the prolonging storage time up to 12 months under the absence or present of antioxidant conditions. The increments of water content in the oils with the addition of PG, BHA and garlic extract are significantly lower than those of without addition of antioxidant at different storage time and temperatures (Figs. 7 & 8). These findings suggested the increased water content of oil are correlated with the changes of acid values and FFA levels, and reflect a gradually oxidation process of oil.

V. Conclusions

The present results suggested that the acid value, FFA and water content in the Jatropha oil increased under different storage time and temperatures compared to the control, but RIP value decreased significantly. The changes of these values in the oils with the addition of PG, BHA and garlic extract may be inhibited compared to those of in the absence of antioxidant during the storage. Our findings suggested that the addition of PG, BHA and garlic extract may prevent the oil oxidation, and maintain the oxidation stability of crude Jatropha oil during the long-term storage. .

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