

Investigations on the Oxidation Stability of Biodiesel Synthesized from Different Vegetable Oils

DIANA CURSARU*, MIHAELA NEAGU, LIANA BOGATU

Petroleum-Gas University Ploiești, 39 București Biv., 100520, Ploiești, România

In the present work, different vegetable oils such as sunflower oil, olive oil, corn oil, peanuts oil, palm oil and grape seeds oil were used as feedstocks for catalytic transesterification with methanol to produce biodiesel. The main drawback of biodiesel is a high susceptibility to oxidation or autoxidation during long-term storage than conventional petrodiesel, because of the presence of varying double bonds in the free fatty acid molecules. The objective of this study was to investigate the oxidation stability of biodiesel by Rancimat method. It was found that oxidation stability of all methyl esters investigated (SFME-Sunflower Oil Methyl Ester, OME-Olive Oil Methyl Ester, CME-Corn Oil Methyl Ester, PME-Peanuts Oil Methyl Ester, PaME-Palm Oil Methyl Ester, GsME-Grape Seed Oil Methyl Ester) did not meet the requirements of EN 14214 (6 hours), therefore the efficiency of two antioxidant additives: ascorbic acid and tert-butylhydroquinone (TBHQ), was investigated on oxidation stability of peanuts oil methyl ester and sunflower oil methyl ester. It was found that both additives improve the oxidation stability of biodiesel but tert-butylhydroquinone is more efficient than ascorbic acid. The physico-chemical properties of vegetable oils and biodiesel such as acid value, density, viscosity, lubricity, cloud point, flash point and heating value were determined according to ASTM standards.

Keywords: biodiesel, oxidation stability, sunflower oil, olive oil, corn oil, peanuts oil, palm oil, grape seeds oil, antioxidants additives

Nowadays, there is a struggle to search alternative renewable energy sources. Biodiesel is a feasible substitute to petroleum-based diesel because possesses inherent lubricity, has lower exhaust emissions than petroleum diesel and its flash point is superior to petroleum-diesel make it safer to handling, transportation and storage [1,2].

Besides being an environmental friendly, nontoxic, with high biodegradability fuel, biodiesel has few disadvantages that make his utilization doubtful in the next future.

Unfortunately, a prohibitive price for feedstocks coupled with poor low temperature properties such as pour point and cloud point, inferior thermo-oxidative stability due to its chemical composition, are important issues that must be overcome in order to increase the viability of biodiesel. Major practical issue facing biodiesel is its susceptibility to oxidation and autoxidation, mainly because of its unsaturated fatty acid chains and the double bonds in the chains of many fatty compounds or because of the air, the presence of light, high temperature or even because of the size of the surface area between biodiesel and air, while the presence of water leads to the hydrolytic degradation of the biodiesel [3].

In literature there are few studies that investigate the possibility to overcome the poor oxidation stability of the biodiesel synthesized from different raw materials [4-12]. The oxidation stability of biodiesel was improved by addition of different additives such as 1,2,3 tri-hydroxy benzene, 3,4,5-tri hydroxyl benzoic acid, 2-tert butyl-4-methoxy phenol [1], 2,6-di-tert-butyl-1,2-dihydroxybenzene, butylated phenol, 2,6-di-tert-butyl-phenol, mono+tri-tert-butyl-phenol [5,13], tert-butylhydroquinone [14], α -tocopherol, N,N'-di-sec-butyl-p-phenylene diamine, butylated hydroxyanisole, butylated hydroxy-toluene, 2,5-di-tert-butylhydroquinone [7].

Several types of vegetable oils, with different fatty acid compositions, have been used as raw materials for biodiesel synthesis. The most investigated were sunflower

[6, 15, 16], soybean [6, 17, 18], rapeseed [6, 19, 20], palm [6, 21], corn [6, 10], olives [6], but non edible oils such as *Jatropha curcas* [8, 12], *Karanja* [11], *Croton Magalocarpus* [1], *Brassica carinata* [2] were not neglected.

In our study we synthesize different fatty acid methyl esters from six vegetable oils (sunflower oil, olive oil, corn oil, peanuts oil, palm oil, grape seeds oil) by catalytic transesterification of the fatty glycerides existing into vegetable oils, in the presence of the methanol by using potassium hydroxide as catalyst, in order to examine the oxidation stability of these esters. Moreover, we study the effect of two antioxidants additives on the oxidation stability of sunflower oil methyl ester and peanuts oil methyl ester. Parallel, it was investigated the evolution of two quality parameters such as acid value and degree of unsaturation (DU) and their correlation with the variation of the oxidation stability.

Experimental part

Materials

Methanol and potassium hydroxide used in our investigation are of analytical grade and were provided by Sigma-Aldrich. Vegetable oils were food-grade. In table 1 are presented the physico-chemical properties of vegetable oils.

Fatty acid methyl esters synthesis

The fatty acid methyl esters were synthesized according to the conventional catalytic transesterification of the fatty glycerides existing into vegetable oils in the presence of methanol by using potassium hydroxide as catalyst via a method detailed elsewhere [22, 23]. The transesterification process was carried out at the following standard conditions: reaction temperature at 60°C, 1 atm. pressure, 6:1 methanol/vegetable oil, 1wt.% potassium hydroxide, 550 rpm stirring speed and 120 min. reaction time.

The crude biodiesel was separated by the phase consisted of glycerol, excess methanol and soap by gravity.

* email: dianapetre@yahoo.com, Tel: + 40 - 244.573 171

Tests	Results						Methods
	S	O	C	P	Pa	Gs	
Density (25°C, kg/m ³)	908	903	913	922	913	925	ASTM D-1298
Viscosity (40°C, cSt)	31.86	34.2	31.98	39.5	35.41	34.5	ASTM D-455
Lubricity WS1.4, (μm)	123	187	220	235	123	114	ASTM D-6079
Acid value (mgKOH/g)	0.12	0.15	0.13	0.11	0.12	0.19	EN 14104
Pour point, (°C)	-13	-10	-18	-6	+16.0	-7	ASTM D-2500

S-sunflower oil, O-olive oil, C-corn oil, P-peanuts oil, Pa-palm oil, Gs- grape seeds oil

Table 1
PHYSICO-CHEMICAL PROPERTIES
OF VEGETABLE OILS

Tests	Results						Methods
	SFME	OME	CME	PME	PaME	GsME	
Density (20°C, kg/m ³)	857	898	902	890	880	912	ASTM D-1298
Viscosity (40°C, cSt)	4.2	4.5	4.5	4.6	4.6	4.2	ASTM D-455
Lubricity WS1.4, (μm)	210	242	232	223	192	195	ASTM D-6079
Acid value, (mgKOH/g)	0.15	0.15	0.15	0.11	0.13	0.26	EN 14104
Pour point, (°C)	-4	-5	-11	+9	+11	-6	ASTM D-2500
Flash point, (°C)	183	176	167	176	169	175	ASTM D-93
Heating value, MJ/kg	33.5	33.8	34.3	33.6	33.5	32.3	ASTM D-975
Cetane number	50	52	51	54	62	48	ASTM D-613
Copper strip corrosion	1	1	1	1	1	1	ASTM D-130

Table 2
PHYSICO-CHEMICAL PROPERTIES OF
METHYL ESTERS

The unreacted catalyst and traces of glycerol and soap were eliminated from crude biodiesel by hot water washing. The residual water in biodiesel was removed by distillation at reduced pressure and 120°C for 30 min [6, 24].

The physico-chemical properties of methyl esters are depicted in table 2.

Rancimat method

Conventionally, the oxidation stability of biodiesel is determined by using Rancimat method according to EN 14214 standard.

The working principle of Rancimat method is depicted in figure 1.

During the measurements a stream of purified air at a flow rate of 10 L/h, is passed through a biodiesel sample (10 mL) kept in a sealed reaction vessel at constant temperature (110 °C). This treatment results in oxidation of biodiesel and the volatile oxidation products are transported in the air stream to a second vessel containing distilled water. The conductivity in the vessel is measured continuously and an oxidation curve is obtained. The time that elapsed until the secondary reaction products appear is called oxidation stability, induction time or induction

period and gives a quantitative measurement of oxidation stability [1, 3, 6].

Analytical method

The fatty acid compositions of biodiesel was analyzed according to EN 14103 standards by using a Varian 450 gas chromatograph with FID detector. The capillary column was a Agilent column with a length of 30 m, a film thickness of 0.25 μm and an internal diameter of 0.32 mm. A 1 μL biodiesel sample was injected using a split ratio (100:1) at 24.65 psi at an inlet temperature of 250°C.

Results and discussions

The fatty acid profile of the methyl esters synthesized in this study is depicted in table 3. The fatty acids from the composition of the biodiesel can be grouped in two categories: monounsaturated (Cn:1) and polyunsaturated with two or three double bonds (Cn:2,3). Based on these compositions Ramos et al. [6] defined a parameter, entitled degree of unsaturation (DU) which was calculated based on the equation 1 and the results are reported in table 3.

$$DU = (\text{monounsaturated Cn:1, wt\%}) + 2 (\text{polyunsaturated Cn:2,3, wt\%}) \quad (1)$$

The degrees of unsaturation together with the acid value give important information about the oxidation stability of

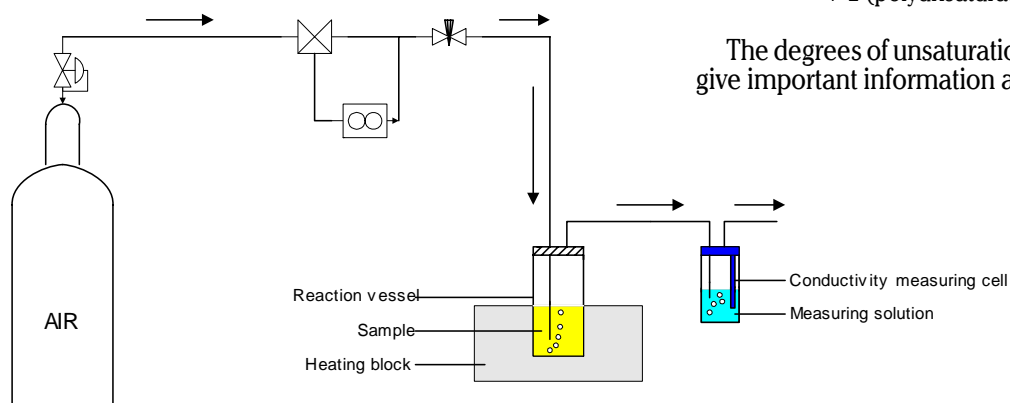


Fig. 1. Principle of Rancimat method

Fatty acids	SFME	OME	CME	PME	PaME	GsME
Lauric, C-12:0	0.0	0.0	0.0	0.0	0.2	0.0
Myristic C-14:0	0.0	0.0	0.0	0.1	1.2	0.1
Palmitic C-16:0	5.8	11.2	12.3	7.6	40.8	6.7
Stearic C-18:0	3.8	1.8	2.6	2.6	5.7	4.2
Oleic C-18:1	28.2	78.4	41.3	58.9	43.3	19.5
Linoleic C-18:2	62.0	8.2	43	30.5	8.6	69.2
Linolenic C-18:3	0.1	0.3	0.8	0.3	0.2	0.3
Other/unknown	0.1	0.1	0.0	0.0	0.0	0.0
DU	152.4	95.4	128.9	120.5	60.9	158.5

Table 3
FATTY ACID COMPOSITION (WT%)
OF BIODIESEL

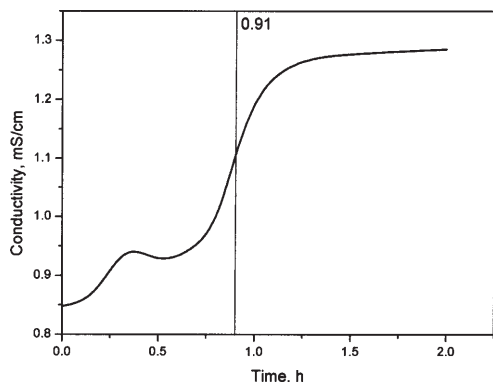


Fig. 2. Oxidation stability of SFME without antioxidants as per Rancimat method

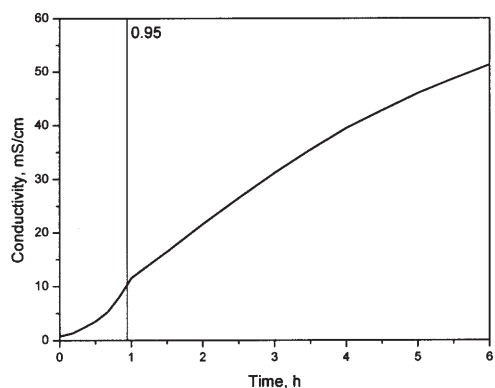


Fig. 3. Oxidation stability of CME without antioxidants as per Rancimat method

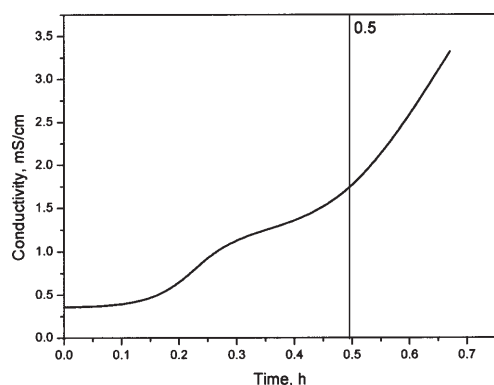


Fig. 4. Oxidation stability of GsME without antioxidants as per Rancimat method

the biodiesel. The oxidation stability decrease with the increase of the content of polyunsaturated methyl esters thus, for higher values of the DU it is expected poor oxidation stability for the corresponding biodiesel. More than that, a higher value of the acid value is the result of the oxidation of the fatty acids methyl esters to fatty acids. During the oxidation process, esters first oxidize to form hydroperoxides and then aldehydes which further oxidize into acids contributing to the increasing of the acid value and furthermore to the degradation of the oxidation stability of the biodiesel [3].

Oxidation stability investigations

In our study the oxidation stability of methyl esters was investigated by using Rancimat method according to EN 14214 standards. By evaluation of the values for DU and for the acid values, it is expected for biodiesel synthesized by vegetable oils rich in linoleic and linolenic acids, such as sunflower, corn or grape seeds oil to have poor oxidation stability, whereas the biodiesel produced from vegetable oil with low polyunsaturated content, such as palm, olives or even peanuts oil to exhibit superior oxidation stability.

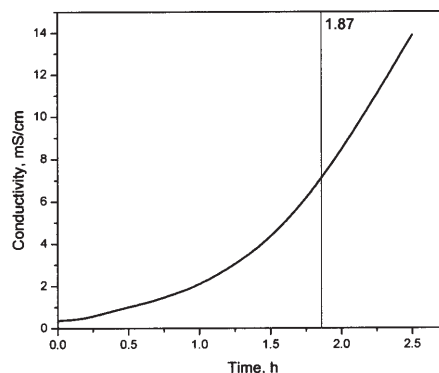


Fig. 5. Oxidation stability of PaME without antioxidants as per Rancimat method

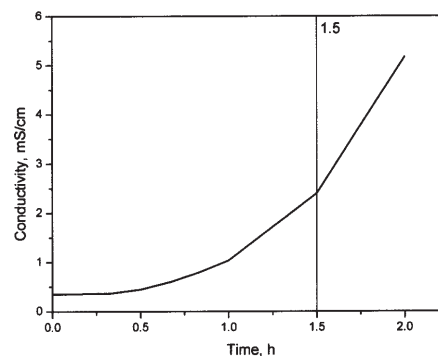


Fig. 6. Oxidation stability of OME without antioxidants as per Rancimat method

The results of our investigations are presented in figures 2-7 and illustrate that different methyl esters without antioxidants additives present poor oxidation stability and the previous expectations have been proved by oxidation tests. In figures from 2-4 are presented the oxidation stability results for sunflower methyl esters, corn methyl esters and grape seeds methyl esters.

These results fitted very well our previous analyses; the poorest oxidation stability (0.5 h) was recorded for grape seeds methyl esters, in fact the ester with the highest degree of unsaturation (158.5) and the highest value for the acid value (0.26 mg KOH/g). By decreasing of the unsaturation degree and acid value was observed that oxidation stability is improved, the induction period for sunflower methyl ester is 0.91 h, while for the corn methyl ester is 0.95 h.

In figures from 5 to 7 are depicted the evolutions of the oxidation stabilities for methyl esters synthesized from vegetable oils with low polyunsaturated content. As expected, it was observed superior oxidation stability for all three methyl esters (palm-1.87 h, olives-1.5 h and peanuts-1.25 h) but not sufficient to overcome the minimum limit of 6 h imposed by the standards.

However, in order to ensure superior quality for biodiesel two of the methyl esters, one with high polyunsaturated content, respectively sunflower methyl ester and the other with low polyunsaturated content, respectively peanuts methyl ester, were selected to be treated with two antioxidant additives to improve their induction period.

As antioxidants additives were selected ascorbic acid and tert-butylhydroquinone.

In figure 8 are presented the results of addition of the sunflower methyl ester with different concentration of both additives.

Addition of the additives seems to be beneficial for sunflower methyl ester because the induction period increases. Tert-butylhydroquinone is more efficient than ascorbic acid, 900 ppm being adequate to overcome the minimum limit of 6 h for the induction period. Unfortunately,

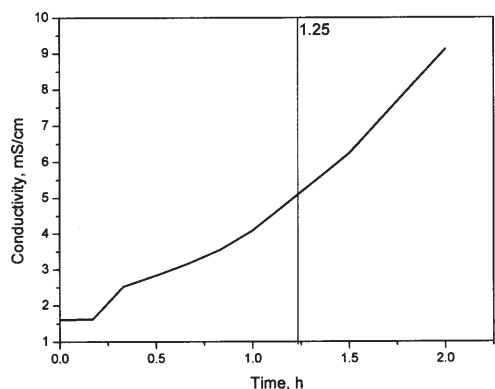


Fig. 7. Oxidation stability of PME without antioxidants as per Rancimat method

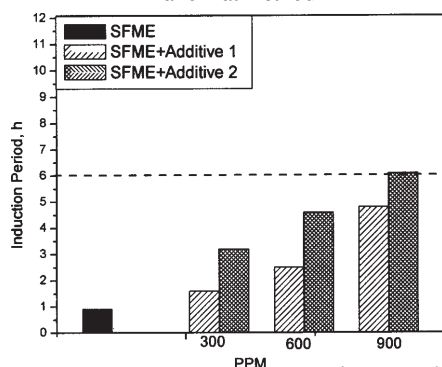


Fig. 8. Influence of ascorbic acid (additive 1) and tert-butylhydroquinone (additive 2) antioxidants on oxidation stability of SFME

for the concentration range studied (300-900 ppm), the ascorbic acid was noncompetitive, the sunflower methyl ester samples additivated with ascorbic acid were found well below the minimum induction period of 6 h.

Figure 9 presents the experimental results obtained with the peanuts methyl ester additivated with different concentration of ascorbic acid and tert-butylhydroquinone.

Tert-butylhydroquinone showed induction period of 6.2 h at 600 ppm while the induction period for 900 ppm of ascorbic acid was 6.1 h. Overall, the effectiveness of these antioxidants was TBHQ > ascorbic acid, in both cases; for esters with low or high polyunsaturated content.

Conclusions

Most of the physico-chemical properties of the synthesized fatty acid methyl esters fulfill the minimum requirements imposed by EN 14214 standards; however the oxidation stability of all methyl esters did not meet the EN 14214 specifications (6 h). In our investigations, Rancimat induction time ranged from 0.5 h recorded for grape seeds oil methyl ester to 1.87 h evidenced for palm oil methyl ester.

The addition of different concentrations of antioxidant additives such as ascorbic acid and tert-butylhydroquinone led to significant increasing of induction time.

Actually, 900 ppm tert-butylhydroquinone was able to satisfy the minimum requirements of oxidation stability of the sunflower oil methyl ester while the ascorbic acid improves the oxidation stability of sunflower oil methyl ester but the concentration range studied (300-900 ppm) is not enough to exceed the inferior limit of the induction period imposed by EN 14214 biodiesel standards.

600 ppm tert-butylhydroquinone and 900 ppm ascorbic acid are adequate to improve the oxidation stability of peanuts oil methyl ester.

In order to avoid possible contaminations of biodiesel that can affect its oxidation stability it is essential to storage

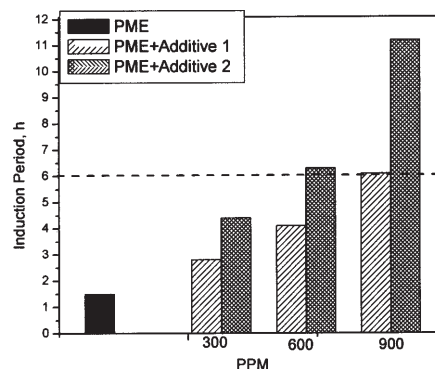


Fig. 9. Influence of ascorbic acid (additive 1) and tert-butylhydroquinone (additive 2) antioxidants on oxidation stability of PME

biodiesel in airtight containers made by mild steel (rust free) at temperatures under 30 °C. Further experiments are required to verify the effectiveness of the antioxidants in terms of induction period for long term storage of biodiesel.

Acknowledgements: The authors are grateful for financial support to Postdoctoral project CNCIS-UEFISCSU PN-RU II 6/2010.

References

- KIVEVELE, T.T., MBARAWA, M.M., BERECZKY, A., LAZA, T., MADARASZ, J., *Fuel Processing Technology* 92, 2011, 1244-1248.
- BOUAID, A., MARTINEZ, M., ARACIL, J., *Bioresource Technology* 100, 2009, 2234-2239.
- KNOTHE, G., *Fuel Processing Technology* 88, 2007, 669-677.
- MCCORMICK, R.L., RATCLIFF, M., MOENS, L., LAWRENCE, R., *Fuel Processing Technology* 88, 2007, 651-657.
- DINKOV, R., HRISTOV, G., STRATIEV, D., ALDAYRI, V.B., *Fuel* 88, 2009, 732-737.
- RAMOS, M.J., FERNANDEZ, C.M., CASAS, A., RODRIGUEZ, L., PEREZ, A., *Bioresource Technology* 100, 2009, 261-268.
- CHEN, Y.H., LUO, Y.M., *Fuel Processing Technology* 92, 2011, 1387-1393.
- JAIN, S., SHARMA, M.P., *Fuel* 90, 2011, 3014-3020.
- KARAVLAKIS, G., HILARI, D., GIVALOU, L., KARONIS, D., STOURNAS, S., *Energy* 36, 2011, 369-374.
- DANTAS, M.B., ALBUQUERQUE, A.R., BARROS, A.K., RODRIGUEZ FILHO, M.G., ANTONIOSI FILHO, N.R., SINFRONIO, F.S.M., ROSENHAIM, R., SOLEDADE, L.E.B., SANTOS, I.M.G., SOUZA, A.G., *Fuel* 90, 2011, 773-778.
- DAS, L.M., BORA, D.K., PRADHAN, S., NAIK, M., NAIK, S.N., *Fuel* 88, 2009, 2315-2318.
- JAIN, S., SHARMA, M.P., *Energy* 36, 2011, 5409-5415.
- KARAVLAKIS, G., STOURNAS, S., KARONIS, D., *Fuel* 89, 2010, 2483-2489.
- BANDIOLI, P., GASPAROLI, A., DELLA BELLA, L., SILVIA, T., *Eur.Lipid Sci. Technol.* 1004,2002, 777-784.
- ANTOLIN, G., TINAUT, F.V., Briceno, Y., CASTANO, V., PEREZ, C., RAMIREZ, A.I., *Bioresource Technology* 83, 2002, 111-114.
- VICENTE, G., MARTINEZ, M., ARACIL, J., ESTEBAN, A., *Ind. Eng. Chem. Res.* 44, 2005, 5447-5454.
- SENSÖZ, S., KAYNAR, I., *Ind. Crop. Prod.* 23, 2006, 99-105.
- XIE, W., PENG, H., CHEN, L., *Appl. Catal. A:Gen.* 300, 2006, 67-74.
- CVENGROS, J., POVAZANEC, F., *Bioresource Technology* 55, 1996, 145-152.
- PETERSON, C.L., REECE, D.L., THOMPSON, J.C., BECK, S.M., CHASE, C., *Biomass Bioenergy* 10, 1996, 331-336.
- KALAM, M.A., MASJUKI, H.H., *Biomass Bioenergy* 23, 2002, 471-479.
- CURSARU, D.L., TĂNĂSESCU, C., *Rev. Chim. (Bucharest)*, **63**, no. 8, 2012, p. 835
- CURSARU, D.L., MIHAI, S., *Rev. Chim. (Bucharest)*, **63**, no. 9, 2012, p. 945
- SARIN, R., KUMAR, R., SRIVASTAV, B., PURI, S.K., TULI, D.K., MALHOTRA, R.K., KUMAR, A., *Bioresource Technology* 100, 2009, 3022-3028.

Manuscript received: 29.11.2012