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BIODIESEL FROM WASTE COOKING OIL: SODIUM CARBONATE MODIFIED SAND AS FILTER, TLC AND THE UNMODIFIED DOMESTIC MICROWAVE OVEN APPROACH

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Abstract: Biodiesel is obtained by transesterification of animal and vegetable triglycerides (fats), and have several advantages over fossil fuel, perhaps the most important being its renewable source and its lack of pollutants such as aromatic and sulfur components. However, biodiesel from vegetable sources such as Soya beans is expensive, and it raises the question of planting for combustibles not for food. The most interesting alternative source for biodiesel is the non expensive waste cooking oil, WCO, which also brings the obvious benefit of transforming a severe pollutant into a green combustible. WCO consists of the triglycerides, but also contains left over food solids, which must be removed by filtration, mono and diglycerides, which are the source of the WCO free fatty acids (FFA), which must be converted to esters before the transesterification of the triglycerides, or, as usually reported, saponification of the final biodiesel mixture will occur. Several methods have been devised to deal with these drawbacks, and generally involve expensive equipment in multistage processes, which include filtration, acid catalysis for the esterification of free fatty acids, removal of the acid catalyst, a base catalyzed transesterification reaction, and, finally, the separation of the glycerol by product and purification of the biodiesel. Herein we propose a new silica gel filtering system, which in one step removes both solids and free fatty acid contents of WCO. In this new approach for biodiesel, an unmodified household microwave oven is used to speed up the base catalyzed transesterification reaction, and a useful piece of advice is given for the easy follow up of the reaction progress by thin layer chromatography.

Keywords: biodiesel; waste cooking oil; microwaves; silica gel.

Resumo: Biodíesel é obtido pela transesterificação de triglicerídios animais e vegetais (gorduras), e possui várias vantagens sobre combustíveis fósseis, talvez o mais importante sendo sua fonte renovável e a falta de poluentes tais como componentes aromáticos ou sulfurados. Entretanto, o biodiesel oriundo de fontes vegetais tal como soja, é caro, e levanta a questão de se plantar por combustíveis e não por comida. A fonte alternativa mais interessante para biodiesel é o óleo de cozinha usado (WCO), que é barato, e que também traz o óbvio benefício de transformar um sério poluente em um combustível verde. WCO é constituído de triglicerídeos, mas também contém restos sólidos de comida, que necessitam ser retirados por filtração, e de mono e diglicerídios, que são as fontes de ácidos graxos livres no WCO, e que precisam ser convertidos a ésteres antes do processo de transesterificação, ou, como sabido, irá ocorrer a saponificação da mistura final do biodiesel. Vários métodos têm sido empregados para lidar com essas inconveniências, e geralmente envolvem equipamentos muito caros em processos de múltiplas etapas, incluindo filtração, catálise ácida para a esterificação dos ácidos graxos livres, remoção do catalisador ácido, a reação de esterificação e, finalmente, a separação do sub produto glicerol e a purificação do biodiesel. Nós estamos propondo um novo sistema de filtração com sílica gel, que em uma etapa remove tanto os sólidos como os ácidos graxos livres do WCO. Nessa nova concepção para biodiesel, um forno de micro ondas caseiro não modificado é utilizado para acelerar a reação de transesterificação base catalisada, e uma dica útil é dada para o monitoramento do progresso da reação por cromatografia de camada delgada.

Palavras-chave: biodiesel, óleo de cozinha usado, micro ondas, sílica gel.

INTRODUCTION

Biodiesel is the methyl or ethyl mono-alkyl esters of long chain fatty acids, which are derived from vegetable oils or animal fat. It can be added to fossil diesel or replace it completely, the advantages being its renewable sources, the better quality of exhaust gas emissions and its biodegradability. Also, if one considers the photosynthetic origin of the vegetable oils, its combustion only restores the previously existing carbon dioxide of the atmosphere [1]. The best starting material for biodiesel is well refined (less than 0.5% free fatty acids, FFA) vegetable oil: under NaOH or KOH catalysis the reaction times are short (up to one hour, typically), and the yields are high [2-4]. However, the use of refined vegetable oils for biodiesel production raises the question of planting for fuel, not for food. Therefore, the use of waste cooking oil (WCO) is the natural alternative, as well as being a way to deal with a large scale pollutant. But WCO have higher amounts of FFA, with which the base catalyst leads to saponification. Therefore, acid catalysis is to be preferred, the drawbacks here being the use of high pressures, excess of alcohol, high cost stainless steel equipments and sulfuric acid effluents, sulfuric acid being the most common catalyst, which is not recovered after the conversion is completed [5-10]. Several attempts have also being made to use enzyme catalysis [11-13], but the lipases seem to be quite sensitive to the alcohol concentration, and the reaction times are quite long, which makes this an overall rather expensive process, albeit WCO may also be employed as starting material in a three-stage process [11]. Combined lipases [14] and fixed bed reactors with immobilized lipases [15] seem however to improve WCO conversion to biodiesel.

There are many efforts to deal with the forthcomings for the low-cost, chemical production of biodiesel, and these include the ingenious idea of using the reusable ferric sulfate [16-17] or poli-ferric sulphate [18] heterogeneous acid catalysis for the initial transformation of high fat content WCO, but the reaction times and high temperatures of the two-stage process still poses a problem. Zeolites have also being used as heterogeneous catalysts to convert WCO into biodiesel, but temperatures up to 450 ^{o}C are necessary [19]. A homogeneous catalyst composed of a superacid $H_3PW_{12}O_{40}.6H_2O$ was reported to produce biodiesel from high fat content WCO at 65 ^{o}C, but at a methanol to oil ratios of 70:1 [20]; partially substituting the protons of that superacid by zinc cations produces nanotube zeolites which work at the same reaction temperatures, but are easier to recover [21]. A mixture of tungsten and aluminum oxides were also used as heterogeneous catalyst, but long reaction times and pretreatment of WCO are required [22]. A solid superacid based in ZrO_2 was proposed, but reaction times up to 4 hours and temperatures up to 120 ^{o}C were necessary to transesterify WCO [23]. Also mixtures of ethanol and methanol aid the transesterification reaction promoted by solid acid catalysts, but still high pressures are necessary, and the yields are only above 80 % [24]. Other mixed oxides of magnesium also require high temperatures and very long reaction times [25-26]. A recent, promising SrO catalyst has been used for the transesterification of WCO with the aid of microwave irradiation [27]. The use of supercritical methanol (up to 560 K) has been proposed as an option for a no-catalyst process [28-29].

While those new approaches are being developed to deal with the FFA content of WCO, authors are still trying to find the optimum conditions for the large scale production of WCO biodiesel from base catalysis, with samples collected from city restaurants [30-35]. There are also proposals of using a two-step KOH/NaOH catalysis to increase the yields of biodiesel from WCO [36]. An earlier attempt to use CaO as an alternative base catalyst failed, due to the poisoning behavior of moisture and the amount of FFA in WCO, apart from partial saponification of the calcium ions [37].

A promising option for the production of biodiesel involves base catalysts and reaction speed up by ultrasound or microwave irradiation. Ultrasonic jets are useful, in the sense that they disrupt the boundaries between the dense WCO and the less dense alcohol with dissolved catalyst phases, avoiding the necessity for vigorous stirring and long contact times. In particular, ultrasound and KOH successfully transformed beef tallow into biodiesel [38]. KOH is also the choice for the transesterification of WCO with methanol in one [39] and two step reactions using continuous reactors [40]. Reaction times of up to 8 minutes were recently reported [41], although NaOH used to increase the catalyst percentage in the mixtures may be lost to soap and increase the difficulty to clean the biodiesel formed [39].

Microwave irradiation (MW) have the advantage over conventional heating in that it delivers energy directly to the reactants, that rapidly rotates, generating heat by molecular friction. In this way, MW accelerates chemical reactions and induces increased yields. However the household microwaves were reported to be modified so that they could be used as biodiesel reactors from WCO [27] [42]. In this paper, we describe a convenient, economically feasible production of ready to use biodiesel from WCO using an unmodified household MW oven. The process is made possible by the pre filtration of the WCO with a silica gel which removes, in one step, solids, FFAs and water from the WCO.

MATERIAL AND METHODS

Materials

The laboratory experiment required an unmodified household microwave oven (2450 GHz/340W), a distillation system, and common laboratory glassware.

Methods

The reaction progress and the complete transformation of mono, di and triglycerides from WCO into monoalkylesters was monitored using Thin Layer Chromatography (TLC) and by proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). TLC experiments were performed using silica-gel coated aluminum foils from Merck, prepared using two drops of acetic acid in 10 mL of a solution of a 95:5 mixture of hexane: ethyl acetate, and samples were taken every 1 minute for 10 minutes. The relevant signals chosen for integration in the ^{1}H NMR experiments were the signal of the α-methylene protons present in all esters derived from triglycerides (2.3 ppm, triplet), as well as the triplet at 2.67 ppm and quartet at 4.10 ppm that indicate the ethyl ester ($–CO_2CH_2CH_3$) formation; the ratio 2:2:3 indicates the complete conversion of the triglycerides into the desired esters.

Characterization and quality control of ethyl biodiesel fuel.

The samples of WCOEEs were sent to the Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil and Derivatives – CEMPEQC, of the Sao Paulo State University at Araraquara, São Paulo, Brazil. Table 1 summarizes the Standard Methods used, as well as the specification limits recommended by the Regulation.The instruments employed in these analyses were an automatic densimeter (Anton Paar GmbH, model DMA4500), a Rancimat® (Metrohm Ion Analysis, model 873), a Pensky-Martens closed cup automatic flash point tester (Petrotest Instruments GmbH, model PMA 4), an automated kinematic viscosity measuring system (Tanaka Scientific Limited, model AKV-202), a micro carbon residue tester (Tanaka Scientific Limited, model ACR-M3), a copper strip corrosion tarnish tester (Petrotest Instruments GmbH), a cold filter plugging point tester (Tanaka Scientific Limited, model AFP-102), an automatic potentiometric titrator (KEM Electronics, model AT-500N2), a coulometric Karl Fischer titrator (Metrohm Ion Analysis, model 756), a gas chromatograph with flame ionization detector (Shimadzu Corporation, model GC-2010) coupled to a CTC Combi PAL headspace and liquid injector system (Shimadzu Corporation, model AOC-5000), an energy dispersive X-ray fluorescence spectrometer

(Shimadzu Corporation, model EDX-800), and an inductively coupled plasma optical emission spectrometer (Thermo Scientific, model iCAP 6300 Duo).

Experimental procedures

Preparation of the silica gel

The procedure for the preparation of the filtering silica follows closely that reported by Prado [43]. 4.0 g of fine construction sand were mixed with 8.0 g of sodium carbonate. The mixture was placed in an oven at 850 ^{o}C for 4 hours. The still hot material was transferred to a sintered glass filter and washed with boiling water. The soluble product was acidified to pH 1 with HCl. The precipitate formed was filtered and placed in an oven at 150 ^{o}C for drying and activation of the silica gel. The crude silica gel is passed through a collection of sieves, and the 60 mesh is retained for the WCO filtration. In this way, 100 mL of WCO can be filtered with this 60 mesh size silica gel, and the filtered oil contains, independently of its origin – animal, vegetable or mixed origin – an acid index of 0.40 mg KOH and a 0.02% acid content.

Preparation of biodiesel

The waste cooking oil (WCO) / Anhydrous ethyl alcohol (99,3%)/ NaOH ratios used in the reactions were 100 mL / 60 mL / 0.80 g respectively.

The crude waste cooking oil (WCO) was filtered through 10.0 g of the prepared silica-gel 60 mesh. The filtered WCO had an acid index of 0.40 mg KOH and a 0.02% water content. The ethanol, previously treated with the required amount of NaOH, was transferred to a beaker containing 100 mL of the filtered oil. This mixture was irradiated in the MW unmodified household microwave oven for 10 minutes at 340 W, the temperature raising to 70 ^{o}C. 10 mL of distilled water was added to the irradiated mixture to help the subsequent separation process. The resulting mixture was transferred to a separation funnel where it formed the waste cooking oil ethyl esters (WCOEEs) upper phase and glycerin (lower phase). After the separation of the phases, the biodiesel was washed with successive additions of 15% by volume of distilled water under moderate agitation until neutral pH, and dried over anhydrous $MgSO_4$; alternatively, water can be distilled off the mixture. The conversion of the triglycerides into WCOEEs was higher than 98%.

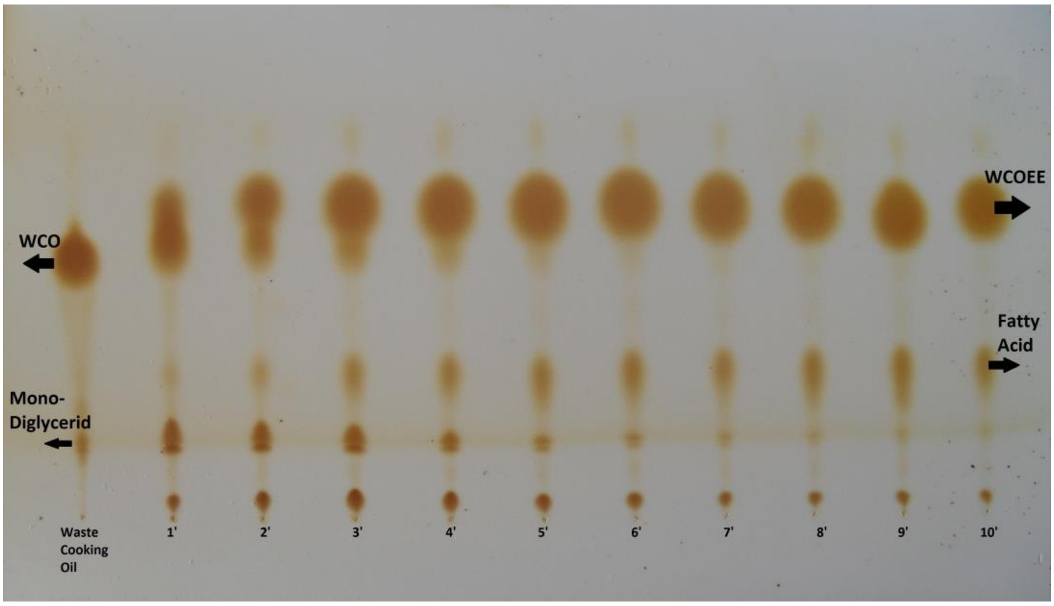
RESULTS AND DISCUSSION

During our study of developing solid catalysts for esterification reactions mediated by microwave irradiation [44-45], our attention was drawn to the transesterification reactions of triglycerides and biodiesel formation. The several drawbacks of this process start with the fact that the triglycerides are poorly soluble in alcohol, which means that either long reaction times or conditions such as high temperatures, high pressures, or microwave or ultrasound reaction enhancement are necessary for good conversions. Against successful transformations there are the dangers of the water content of the triglycerides, for it causes saponification, which consumes the catalysts and inhibits the products glycerol/ester separation. The presence of free fatty acids is also a problem, because they are gelatinous solids and poison the catalyst by forming fatty acid salts. All these factors point to the best raw material for biodiesel from transesterification reactions to be well refined vegetable oils, which in turn makes the production of the new fuel a non economical process. In the literature, there appeared several articles dealing with microwave assisted transesterification of pure vegetable oils [46-49], but still, there are strong ethic arguments against their uses, such as planting for fuel, not for food. At least one of these publications had to do with the transformation of waste frying palm oil into biodiesel [42] and one which used WCO [27], but the microwave reactors had to be specially modified for the reaction purposes [42] or to improve the security of the process due to the high output power used [27]. Waste cooking oil is very appealing as the feedstock choice for biodiesel, partially because it is renewable, partly because of its low or no cost, but principally as the alternative to transform a large scale pollutant into a greener fuel. However, on top of the reaction drawbacks mentioned earlier, used cooking oils are also rich in solid left overs from cooking. All these arguments lead to a reaction scheme that begins with a WCO filtration step, followed by a time and energy consuming drying process and an acid catalyzed transformation of the FFA content to esters, before going on to the proper microwave enhanced transesterification reaction. These combined production steps obviously tend to increase the price of the biofuel.

It seemed appropriate therefore to begin our study with the first filtration step for the future use of WCO, and silica gel seemed to be an appropriate filtering agent, because of its basic capacity to retain humidity, the first enemy of the fast, economic, base catalyzed transesterification. Also, the polar, hydroxyl nature of its surface makes it appropriate to retain any FFA which would tend to pass through the filter, due to its gelatinous nature. Moreover, the size of the silica gel particles can be chosen so that it can retain solid particles with ease. After several filtration attempts with different types of silica gels, a particular sodium carbonate modified silica seemed to fulfill well all the requirements at once. In this way, independently of its origin, 100.0 mL of WCO, when passed through 10.0 g of this carbonate treated silica, present FFA and water contents well within the limits for optimum base catalyzed transesterifications, permitting therefore the production of crude biodiesel in a two stage process.

For the MW enhanced transesterification step, the irradiation time chosen to convert 100.0 mL of WCO was 10 minutes. It is a fact that the reaction can be finished in 3 minutes under higher MW power, but the electrical fields of household MW ovens are inhomogeneous and can cause hotspots. Longer reaction times and lower MW potencies randomize these effects, ensuring the smooth completion of the reaction. Lower potencies also minimize the loss of alcohol by evaporation inside the microwave cavity.

The thin-layer chromatography TLC) used to follow-up the transesterification process, Figure 1, show clearly the quality of the WCO as it is obtained after the filtration with the carbonate modified silica gel. For instance, it shows that it contains a small fraction of mono and diglycerides, and that the content of FFAs is negligible prior to MW irradiation. It shows also the total absence of glycerin, which will appears as the bottom spot in the TLC plate after irradiation commences. Indeed, the appearances of the glycerin and biodiesel spots are the evidence that the reaction starts at the very beginning of MW irradiation. As from the first minute of irradiation, there appears in the TLC plate the presence of FFAs, which must have been formed by the residual water content; the consumption of that residual water means that it can no longer sustain the hydrolysis of the formed biodiesel. After the sixth minute is also evident from the TLC plate of the transformation of the mono and diglycerides into biodiesel, so that, by the end of the reaction, only glycerin, biodiesel and the small, but unavoidable amount of FFA, result.



- Figure 1. Thin Layer Chromatography (TLC), using silica gel coated aluminum foils from Merck and a mixture of hexane: ethyl acetate (95:5).

The effect of the amount of catalyst on WCOEEs production was studied in experiments with different concentrations of NaOH (0g, 0.5g, 0.75g, 0.80g, 0.90g, 1.00g, 1.10g) of NaOH, each experiment repeated five times. As expected, no product appeared with 0% catalyst. Catalyst concentrations higher than 1.10% adversely affected WCOEEs production by the formation of fatty acids and resulting in soap formation. At concentrations below 0.80g the amount of catalyst is not enough to ensure complete conversions.

The optimum yield of WCOEEs was gained at an ethanol/oil volume ratio of 6:10. At ethanol-to-oil volume ratios greater than that, the separation of esters from glycerol was more difficult. Unreacted ethanol suppresses the gravity decantation and traces of glycerol remain in the biodiesel phase. For comparison purposes, similar tests using the optimized parameters, took typically about 120 minutes to be completed under reflux conditions. The separation of the biodiesel from glycerol can be accelerated by centrifugation, but it proceeds quite well in a common separation funnel.

Characterization and Quality Control of WCOEEs

The samples of WCOEEs were tested to determine the ethyl biodiesel the quality according to ASTM, EN, and NBR Standard Methods established by ANP Regulation 7. Table 1 shows the specification limits of the standard methods and the WCOEEs results obtained for each requirement. Comparison of our results with those for similar biodiesels obtained by conventional, alkaline ethanolysis with reflux induced methods, indicate that MW irradiation produces a somewhat superior fuel at least where it is compared the carbon residues after the fuel consumption; Encinar et al. [50] found, following the reflux method 0.14 to 0.15% of these residues, whereas our tests detected no residues at all, Table 1.

Table 1. Biodiesel Fuel Physicochemical Properties of Waste Cooking Oil Ethyl Esters (WCOEEs).

Physical and Chemical Properties	Units	Standard Method	Specification Limits ANP Regulation 7	WCOEEs
Relative Density @ 20 ºC	kg/m^3	ASTM D4052	850.0 – 900.0	879.4
Water Content, max.	mg/kg	ASTM D6304	500.0	397.6
Flash Point, min.	ºC	ASTM D93	100.0	100.0
Oxidative Stability @ 110 ºC, min	H	EN 14112	6.0	1.5
Kinematic Viscosity @ 40 ºC	mm^2/s	ASTM D445	3.0 – 6.0	4.4
Carbon Residue, Max	mass %	ASTM D4530	0.050	0.0
Copper Corrosiveness, 3 h @ 50 ºC, max	-	ASTM D130	1A or 1B	1A
Cold Filter Plugging Point, max	ºC	ASTM D6371	19.0	- 1.0
Total Acid Number, max	mg KOH/g	ASTM D664	0.50	0.098
Iodine Value	g/100g	EN 14111	NA*	87.8
Monoglycerides	mass %	ASTM D6584	NA*	0.80
Diglycerides			NA*	0.50
Triglycerides			NA*	0.30
Free Glycerin, max			0.02	0.01

Total Glycerin, max			0.25	0.20
Methanol or Ethanol, max	mass %	EN 14110	0.20	0.019
Methyl or Ethyl Esters, min	mass %	EN 14103	96.5	97.4
Sodium + Potassium, Max	mg/kg	NBR 1553	5.0	1.7
Calcium + Magnesium, max	mg/kg		5.0	0.1
Phosphorus, max	mg/kg		10.0	0.5
Total Sulfur, Max	mg/kg	according to ASTM D4294	50.0	39.0

* NA – not applicable

CONCLUSION

Waste cooking oil, WCO, of various origins can be properly and adequately filtered through a new silica gel prepared from construction sand and sodium carbonate. The filtrate is a WCO free from water, glycerin and FFAs, and therefore, ready to be used in base catalyzed transesterification reactions. Using this clean WCO, biodiesel of excellent quality is obtained in a 10 minutes reaction, mediated by low power MW irradiation using a conventional, unmodified house MW oven. The entire transesterification reaction is easily and completely followed by thin layer chromatography.

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REFERENCES

[1] B. K. Barnwal, M. P. Sharma, Renew. Sust. Energy Rev. 9 (2005) 363–78.

[2] P. R. Muniyappa, S. C. Brammer, H. Noureddini, Bioresour. Technol. 56 (1996) 19–24.

[3] M. P. Dorado, E. Ballesteros, F. J. Lopez, M. Mittelbach, Energy Fuel 18 (2004) 77–83.

[4] G. Antolín, F. V. Tinaut, Y. Briceno, V. Castano, C. Perez, A. I. Ramirez, Bioresour. Technol. 83 (2002) 111–4.

[5] Y. Zhang, M. A. Dube, D. D. McLean, M. Kates, Bioresour. Technol. 2003;89:1–16.

[6] M. I Al-Widyan, A. O Al-Shyoukh, Bioresour. Technol. 85 (2002) 253–6.

[7] G. M. Tashtoush, M. I. Al-Widyan, A. O. Al-Shyoukh, Energy Convers. Manage. 45 (2004) 2697–711.

[8] M. Canakci, J. Van Gerpen, Trans. ASAE 46 (2003) 945–54.

[9] Y. Zhang, M. A. Dube, D. D. McLean, M. Kates, Bioresour. Technol. 90 (2003) 229–40.

[10] H. A. Farag, A. El-Maghraby, N. A. Taha, Fuel Process. Technol. 92 (2011) 507-510.

[11] Y. Watanabe, Y. Shimada, A. Sugihara, Y. Tominaga, JAOCS 78 (2001) 703–7.

[12] Y. Watanabe, Y. Shimada, A. Sugihara, H. Noda, H. Fukuda, Y. Tominaga, JAOCS 77 (2000) 355–60.

[13] Y. Watanabe, Y. Shimada, A. Sugihara, Y. Tominaga, J. Mol. Catal. B: Enzym 2002;17:151–5.

[14] Y. Liu, Y. Yan, F. Hu, A. Yao, Z. Wang, F. Wei, AIChE J 56 (2010) 1659-16655.

[15] Y. Chen, B. Xiao, J. Chang, Y. Fu, P. Lv, X. Wang, Energy Convers. Manage. 50 (2009) 668-673.

[16] Y. Wang, S. Ou, P. Liu, Z. Zhang, Energy Convers. Manage. 48 (2007) 184-188.

[17] P. D. Patil, V. G. Gude, S. Deng, Ind. Eng. Chem. Res. 48 (2009) 10850-10856.

[18] Y. Wang, J. Nie, M. Zhao, S. Ma, L. Kuang, X. Han, S. Tang, Energy Fuels 24 (2010) 2104-2108.

[19] A. Brito, M. E. Borges, M. Otero, Energy fuels 21 (2007) 3280-3283.

[20] F. Cao, Y. Chen, F. Zhai, J. Li, J. Wang, X. Wang, S. Wang, W. Zhu W, Biotechnology and Bioengineering 101 (2008) 93-100.

[21] J. Li, X. Wang, W. Zhu, F. Cao, $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ ChemSusChem 2 (2009) 177-183.

[22] C. Komintarachat, S. Chuepeng, Ind. Eng. Chem. Res. 48 (2009) 9350-9353.

[23] B. Fu, L. Gao, L. Niu, R. Wei, G. Xiao, Energy Fuels 23 (2009) 569-572.

[24] M. K. Lan, K. T. Lee, Fuel Process. Technol. 92 (2011) 1639-1645.

[25] M. A. Olutoye, B. H. Hameed, Bioresour. Technol. 102 (2011) 3819-3826.

[26] Z. Wen, X. Yu, S-T. Tu, J. Yan, E, Dahlquist, Bioresour. Technol. 102 (2010) 9570-9576.

[27] M. Koberg, R. Abu-Much, A. Gedanken, Bioresour. Technol. 102 (2011) 1073-1078.

[28] A. Demirbas, Energy Convers. Manage. 50 (2009) 923-927.

[29] P. Patil, S. Deng, J. I. Rhodes, P. J. Lammers, Fuel 89 (2010) 360-364.

[30] X. Meng, G. Chen, Y. Wang, Fuel Process. Technol. 89 (2008) 851-857.

[31] L. F. Bautista, G. Vicente, R. Rodríguez, M. Pacheco, Biomass Bioenergy 33 (2009) 862-872.

[32] C. B. H. Chua, H. M. Lee, J. S. C. Int. J. Life Cycle Asses. 15 (2010) 417-423.

[33] P. Kumaran, N. Mazlini, I. Houssein, M. Nazrain, M. Khairul, Energy 36 (2011) 1386-1393.

[34] A. B. Chhetri, K. C. Watts, M. R. Islam, Energies 1 (2008) 3-18.

[35] T. Sakai, A. Kawashima, T. Koshikawa, Bioresour. Technol. 100 (2009) 3268-3276.

[36] G. Çayli, S. Küsefoglu, Fuel Process. Technol. 89 (2008) 118-122.

[37] M. Kouzu, S. Yamanaka, T. Kazuno, M. Tajika, Y. Aihara, Y. Sugimoto, J. Hidaka, J. Japan Petrol. Inst. 50 (2007) 79-86.

[38] L. S. G. Teixeira, J. C. R. Assis, D. R. Mendonça, I. T. V. Santos, P. R. B. Guimarães, L. A. M. Pontes, J. S. R. Teixeira, Fuel Process. Technol. 90 (2009) 1164-1166.

[39] S. H. Hingu, P. R. Gogate, V. K. Rathod, Ultrason. Sonochem. 17 (2010) 827-832.

[40] L. T. Thanh, K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, H Bandow, , Bioresour. Technol. 101 (2010) 5394-5401.

[41] X. Fan, X. Wang, F. Chen, Fuels Energ. Sci. J. 3 (2010) 23-27.

[42] V. Lertsathapornsuk, R. Pairintra, K. Aryusuk, K. Krisnangkura, Fuel Process. Technol. 89 (2008) 1330-1336.

[43] A. G. S. Prado, E. A. Faria, P. M. Padilha, Quim. Nova 28 (2005) 544-547.

[44] S. L. Barbosa, M. J. Dabdoub, G. R. Hurtado, S. I. Klein, A. C. M. Baroni, C. R. Cunha, Applied Catalysis A: General 313 (2006) 146–150.

[45] S. L. Barbosa, G. R. Hurtado, S. I. Klein, V. L. Junior, M. J. Dabdoub, C. F. Guimarães, A. C. M. Baroni, Applied Catalysis A: General 338 (2008) 9–13.

[46] T. M. Barnard, N.E. Leadbeater, M. B. Boucher, L. M. Stencel, B. A. Wilhite, Energy Fuels 21 (2007) 1777-1778.

[47] N. E. Leadbeater, L. M. Stencel, Energy Fuels 20 (2006) 2281-2283.

[48] M. Z. Duz, A. Saydut, G. Ozturk, Fuel Process. Technol. 92 (2011) 308-313.

[49] S. Zhang, Y.G. Zu, Y. J. Fu, M. Luo, D. Y. Zhang, T. Efferth, Bioresour. Technol. 101 (2010) 931-936.

[50] J.M. Encinar, F. Jua, J. F Gonzalez, A. Rodriguez-Reinares, Fuel Process. Technol. 88 (2007) 513-522.