

Study of an Innovative Process for the Production of Biofuels using Non-edible Vegetable Oils

Max J. A. Romero^a, Andrea Pizzi^b, Giuseppe Toscano^b, Barbara Bosio^a,
 Elisabetta Arato^{*a}

^aDICCA, Department of Civil, Chemical and Environmental Engineering, University of Genoa. Via Opera Pia, 15, 16145 Genoa, Italy.

^bD3A, Department of Agricultural, Food and Environmental Sciences, Polytechnic University of Marche. Via Brecce Bianche 10, 60131 Ancona, Italy.
 Elisabetta.arato@dicat.unige.ext

In recent years, several strategies have been used to mitigate the impact of greenhouse gases, one of which is the production of liquid biofuels, where different processes have been employed such as pyrolysis, transesterification, and more recently the process of catalytic hydrotreatment. The latter was adopted to obtain a biofuel with better properties: higher heating value, lower density and better flow properties in cold than biodiesel. However also the catalytic hydrotreatment presents significant disadvantages: the use of hydrogen and the use of conventional catalysts composed of metal sulphides. On the basis of these considerations, our group is studying the deoxygenation of triglycerides through the innovative process of decarboxylation, in which the atoms of oxygen contained in the biomass are removed in the form of carbon dioxide which can then be captured. The decarboxylation process does not require the use of expensive reagents such as hydrogen or noble metal catalysts.

For this work we selected the *Jatropha Curcas* oil as a model of non-edible oil. After our tests was possible to obtain a liquid biofuel with a high composition of hydrocarbons, around 81 %, formed mainly of C8-C15 hydrocarbons. This product also showed good properties as an heating value around 44 MJ/Kg, higher than biodiesel (39 MJ/Kg) and diesel (43 MJ/Kg), and a lower viscosity (4.2 cSt) compared to the biodiesel (4.4 cSt). The yields obtained for the overall process were greater than 80 %.

1. Introduction

Over the years different strategies have been used to mitigate the impact of greenhouse gases, such the production of liquid biofuels. For instance, the thermal and catalytic cracking (pyrolysis) is a simple process capable of supplying a bio-oil from renewable feeds. However this process is highly unselective and also yields a number of undesirable compounds, mainly oxygenates. Other way for obtain a liquid biofuels from renewable feeds is using the transesterification process, a well-established technology. The transesterification is the reversible reaction of fats or oils with an alcohol to form fatty acid methyl esters (FAME) known as biodiesel and glycerol. According to Na et al. (2012) it was verified that the biodiesel has some drawbacks such as low energy content and high cloud point. Morgan et al. (2012) adds that biodiesel has poor storage stability, high emissions of NO_x and tendency to form deposits in the fuel injection systems.

As it is evidenced by Santillan-Jimenez et al. (2013) not long ago the catalytic hydrotreating has been adopted for obtain a biofuel with better properties. It has a higher energy density, lower density and better flow properties in cold compared to biodiesel, it is virtually identical to conventional diesel, but with a higher cetane number. Its principal characteristic is that can be used as 100 % fuel. Chistyakov et al. (2013) reported the direct conversion of rapeseed oil to alkanes-aromatics fraction of hydrocarbons C₃-C₁₁ that may be considered as high-octane additive to gasoline through catalytic hydrotreating. However the technology also has important drawbacks, principally the expensive use of hydrogen and the use of conventional catalysts based in metal sulphides.

On the basis of these considerations, our group is studying the deoxygenation of triglycerides through an alternative and innovative process known as decarboxylation, in which the atoms of oxygen contained in the biomass are removed in the form of carbon dioxide which later can be stored.

On this topic some studies have been conducted analysing the deoxygenation of fatty acids and their derivatives using metal catalysts supported in a semi-batch process. Snåre et al. (2006) have analysed the deoxygenation reaction of stearic acid over different catalysts in order to obtain the most promising metal and support combination. Palladium supported on activated carbon has been found to be a particularly effective catalyst for this purpose, followed by platinum and nickel. In the work of Mäki-Arvela et al. (2007) very high yields of n-heptadecene (97 %) were achieved in the decarboxylation of stearic acid over the Pd/C catalyst at 300 °C under helium atmosphere. According to Morgan et al. (2010) it is necessary to avoid the use of noble metals as catalysts for their high cost from an industrial standpoint, having this in mind they have studied the use of nickel. The Ni has showed highly active compared to Pd or Pt supported on activated carbon. Given the results of Ni for this application, especially in view of its low cost, Morgan et al. (2012) have extended their studies to include Ni supported on alumina. On the other hand, with the same aim, Na et al. (2010), have tested the decarboxylation of oleic acid, using hydrotalcites instead of precious metals in a batch process. Oleic acid conversions were more than 98 % and the oxygen content in the reaction product was less than 1 wt% in the case of decarboxylation with MG63 (63 % of MgO) and MG70 (70 % of MgO) at 400 °C. Na et al. (2012) carried out in a second step the catalytic decarboxylation of pyrolysis oil from *Chlorella* sp. KR-1 cells over hydrotalcite MG63 (63% of MgO). In this case the product yield at a reaction temperature of 400 °C was 79 % and the degree of oxygen removal was 78%. The diesel fraction in the product obtained under the given reaction condition was 84 %.

The recent literature evidences that the different catalysts studied are effective in deoxygenation through the decarboxylation of model acids, however there are not many studies that indicate the decarboxylation of triglycerides. In this work we present the results concerning to the deoxygenation through decarboxylation of the *Jatropha Curcas* oil used as a model of non-edible oil. According to Gillani et al. (2013) *Jatropha* plant could have a lot of advantages such as growing in lower irrigated and wild areas with lesser soil/fuel management requirement. As this is a non-edible plant so therefore unfit for human consumption and would not be a threat for the food concurrence in the first place. Other non-edible oils as waste vegetable oil, residual fats and bio-oil from residual solid biomass also are interesting raw materials that can be studied. The tests were carried out using a bench top stirred reactor and using alumina and a type of hydrotalcite (MG70) as catalysts, operating at temperatures of 350 °C and 400 °C. The hydrotalcite has been considered of due to its strong basicity. As it is referenced by Martins M. et al. (2013) hydrotalcite consists of a natural anionic clay containing carbonate anions intercalated between lamellar double hydroxide, magnesium and aluminium. The lamellar double hydroxides, although not abundant in nature, can be synthesized in the laboratory at a relatively low cost.

2. Deoxygenation experiments and analysis equipment

The different tests on *Jatropha Curcas* oil deoxygenation were performed in a mechanically stirred 500 mL reactor (model 4575A – PARR Instrument Company) operating in a batch mode. In a typical experiment around 180 g of *Jatropha Curcas* oil and 3 % of catalysts were added in the reactor. Additionally the *Jatropha Curcas* oil deoxygenation was tested also without using catalyst. Before each experiment, the reactor was purged with nitrogen for 3 min in order to remove the remaining oxygen and was pressurized to 3 bar approximately. Then the stirring was started and the temperature was increased to 350 °C and 400 °C, maintaining these levels for 3 h and 6 h depending on the test carried out. When the test finished the reactor cooling system, based on the external water circulation, was used to decrease the temperature down to room temperature. The gas produced in the reaction was taken in special bags to facilitate the gas chromatography analysis. The liquid products were weighed to determine the mass yields and successively stored in small plastic containers until analyses.

The instrument used in GC analysis was an Ultra Trace GC (Thermo Finnigan, Milan, Italy) equipped with a ZB-WAX capillary column (30 m x 0.32 mm x 0.50 µm). The initial temperature for the analysis was programmed at 150 °C (hold time 2 min), with successive increase of 3 °C/min up to 175 °C (hold time 1 min), with final increase of 2 °C/min until the final temperature of 210 °C was reached. Additionally the composition of the products was determined using a GC/MS (Focus-ISQ ThermoScientific) equipped with TG-SQC column (15 m x 0.25 mm x 0.25 µm). The starting temperature was calibrated at 70 °C (hold time 5 min), with an initial increase of 5 °C/min up to 130 °C (hold time 1 min), then a second ramp of 5 °C/min up to 270 °C (hold time 1 min), and a final ramp of 25 °C/min up to 320 °C (hold time 5 min). While kinematic viscosity (at 40 °C) and the heating value were analyzed in compliance with UNI EN ISO 3104:2000 and ASTM D240-09, respectively. On the other hand the gaseous products were analyzed

using a gas chromatograph Chrompack MICRO-GC CP 2002 equipped with a microTCD detector and two parallel columns: the first a PoraPLOT Q column used for analyzing the CO₂ and light hydrocarbons (CH₄ excluded), the second a CP-Molsieve 5A column for analyzing the H₂, O₂, CH₄ and CO.

3. Results and discussion

3.1 Characterization of the *Jatropha Curcas* oil

The triglycerides composition of the *Jatropha Curcas* oil was determined using a GC analysis from their corresponding fatty acid methyl esters obtained by transesterification. The *Jatropha Curcas* oil resulted composed of methyl stearate and methyl palmitate derivatives from stearic acid and palmitic acid respectively (saturated fatty acids) in around of 41 %. While methyl linoleate and methyl linolenate derived from linoleic acid and linolenic acid (polyunsaturated fatty acids) are present in a quantity of 30 %. The amount of methyl oleate derived from oleic acid (monounsaturated fatty acid) is of 29 %.

3.2 Chemical properties of the products

As a result of the various tests it was obtained that, when 350 °C was used as reaction temperature, the yield of liquid products is higher compared to 400 °C, as reported in Table 1. The GC analysis performed on the different products showed that in all cases the triglycerides conversion was 100 % regardless of the reaction temperature used. A detailed analysis with GC-MS spectrometry has allowed to identify the composition of these products. The Table 1 reports also the composition of the liquid products obtained under different reaction conditions. At 350 °C per 3 h the composition of these products is not satisfactory. In particular, at this temperature and in the absence of catalyst, the total amount of hydrocarbons in the liquid product is not greater than 9 % and the acid composition is around 60 %. While the use of alumina or hydrotalcite as catalysts seems not promoting the reaction, indeed the amount of products is lower and these are characterized by a higher percentage of acids.

Table 1: Composition of the products obtained under different reaction conditions according to GC/MS analysis

Test	Yield (% wt.)	Composition of the products obtained - GC/MS Peak Area (%)					
		Hydrocarbons	N	CO	Oxygenated	Acids	Other compounds
No Catalyst, 350 °C, 3 h	93.85	8.65	17.91	7.01	5.71	60.75	0.00
No catalyst, 400 °C, 3 h	85.83	70.96	6.77	3.83	4.32	10.86	2.98
Hydrotalcite, 350 °C, 3 h	88.63	4.92	3.94	10.68	18.12	61.82	0.50
Hydrotalcite, 400 °C, 3 h	83.25	68.43	1.13	1.02	26.24	0.40	2.50
Hydrotalcite, 400 °C, 6 h	81.43	81.08	1.75	0.73	12.94	0.00	3.52
Alumina, 350 °C, 3 h	91.85	5.08	3.66	7.84	9.18	73.99	0.45
Alumina, 400 °C, 3 h	83.70	64.96	0.69	0.00	11.56	18.68	4.12

On the other hand, when 400 °C were used as reaction temperature, better results were obtained: when no catalyst was used the total composition of hydrocarbon was above 70 %, and of this percentage the content of hydrocarbons with a number of carbon atoms per molecule between C8 and C17 was around 61% as reported in Figure 1. Although the product contains acids in around 11 % and traces of nitrogen and carbon monoxide. Using alumina as catalyst the process seems not to be favoured: the formation of hydrocarbons, around 65 % (52 % corresponding to C8-C17 hydrocarbons), is lower than when no catalyst was used and the presence of acids is about 19 %.

However best results were obtained with the use of hydrotalcite: the composition of the product after 3 hours treatment is approximately 68 % of hydrocarbons (mainly paraffinic hydrocarbons), 52 % corresponds to hydrocarbons with a number of carbon atoms per molecule between C8 and C17 and acids or carbon monoxide are absent. Even better results were obtained when the reaction time was increased from 3 h to 6 h. In this case was found a total amount of hydrocarbons around the 81 % and hydrocarbons C8-C15 increases approximately by 9 %. While the quantity of hydrocarbons C16-C17 remains approximately constant, and the heavy hydrocarbons C18 + increase only by 3 %. Another interpretation of the results obtained by the GC-M spectrometry evidences that the products obtained at 400 °C were mainly composed by saturated hydrocarbons: alkanes and cycloalkanes. At this temperature, the products obtained with the use of hydrotalcite showed a slight presence of aromatics, the result is shown in Table 2. The composition in hydrocarbons of the biofuel obtained is similar to the composition of the diesel or biofuel produced through catalytic hydrotreatment and evidently it is different from the biodiesel that is a

mixture of methyl esters of fatty acids (which contain oxygen atoms in their structure). The deoxygenation of the *Jatropha Curcas* oil and the subsequent formation of paraffinic hydrocarbons is attributed to the fact that reactions as decarbonylation, decarboxylation and hydrogenation removed the atoms of oxygen contained in the biomass mainly in the form of carbon dioxide and carbon monoxide. But also other reactions such as dehydrogenation, isomerization, cyclization, dimerization and cracking are presents in the process as Snåre et al. (2006) have reported in the production of linear hydrocarbons from fatty acids. The results obtained at 400 °C are consistent with the results obtained by Na et al. (2012) when tested the catalytic decarboxylation of pyrolysis oil from *Chlorella* sp. KR-1 cells using hydrotalcite MG63 (63 % of MgO) at the same temperature. They obtained a liquid product yield of 79% and the results of the major compounds in that product, according to the GC-MS peak areas, showed a composition of C10-C17 hydrocarbons of around 42 %.

3.3 Physical properties of the products

On the other hand when the reaction was conducted at 350 °C the calorific values measured were of the order of 40 MJ/Kg and all products had a semi-solid consistency at room temperature. At 400 °C and without the use of a catalyst the process allows the reduction of the oil viscosity up to about 6 cSt and the obtainment of a calorific value of about 43 MJ/Kg in the final product. The viscosity increases to 10 cSt when the alumina is used as catalyst and the calorific value is reduced to about 42 MJ/Kg. The hydrotalcite used as catalyst for 3 h test provided an equal viscosity of the alumina case, that is around 10 cSt, and a heating value of 43 MJ/kg. Increasing the reaction time from 3 h to 6 h, the viscosity of the biofuel obtained was equal to 4 cSt, that is lower than the biodiesel viscosity obtained from *Jatropha Curcas* oil (around 4.5 cSt) and near to the diesel EN 590 (around 3.5 cSt), while the obtained heating value of about 44 MJ/kg was much higher than the heating value of the biodiesel from *Jatropha Curcas* oil (around 39 MJ/kg) and higher than the heating value of the Diesel EN 590 (around 43 MJ/Kg). Additionally such value is near to the heating value of the biofuel obtained through catalytic hydrotreatment (around 44 MJ/kg).

Table 2: Type of hydrocarbons in the different products, according to GC/MS analysis

Test	Hydrocarbons in the products GC/MS peak areas (%)	Composition of the products obtained - GC/MS Peak Area (%)					
		Saturated		Unsaturated		Aromatic Others	
		Alkane	Cycloalkane	Alkene	Alkyne		
No Catalyst, 350 °C, 3 h	8.65	100.00	0.00	0.00	0.00	0.00	0.00
No catalyst, 400 °C, 3 h	70.96	87.32	4.89	5.27	0.61	1.41	0.49
Hydrotalcite, 350 °C, 3 h	4.92	81.10	18.90	0.00	0.00	0.00	0.00
Hydrotalcite, 400 °C, 3 h	68.43	88.42	5.18	2.94	0.00	2.59	0.87
Hydrotalcite, 400 °C, 6 h	81.08	84.90	4.69	2.74	1.88	3.52	2.33
Alumina, 350 °C, 3 h	5.08	86.32	8.86	4.81	0.00	0.00	0.00
Alumina, 400 °C, 3 h	64.96	85.09	6.37	3.47	2.72	2.92	0.98

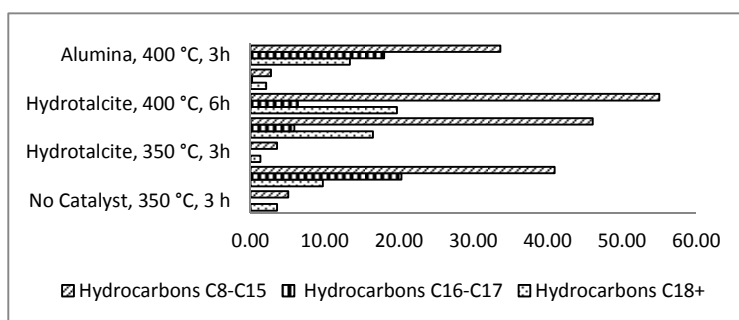


Figure 1: Principal compounds found in the gaseous products when tests were carried out at 400 °C

3.4 Gaseous products

For a better understanding of the way through which the oxygen is eliminated from the triglycerides, gaseous products were subjected to GC analysis. In the Figure 2 we can see the composition of the gaseous products. It was verified that the main compounds in the gaseous products of the different samples, at 400 °C, were CO and CO₂. The presence of CO can possibly be attributed to the reverse water-gas shift reaction. Methane, ethane, oxygen and hydrogen were also present in the reaction gas. The formation of methane could be the result of the hydrogenation of CO or CO₂ however, they could also be produced from a cracking reaction. Snåre et al. (2006) consider that the fact that hydrogen is not used in the reaction system does not necessarily imply that hydrogen is absent. It is possible that hydrogen can be provided in situ by the solvent or by other organic compounds on the catalyst surface or by the surface itself if the catalyst is reduced under H₂ before its use. Light hydrocarbons as methane, propane and propylene were also identified as a minor products.

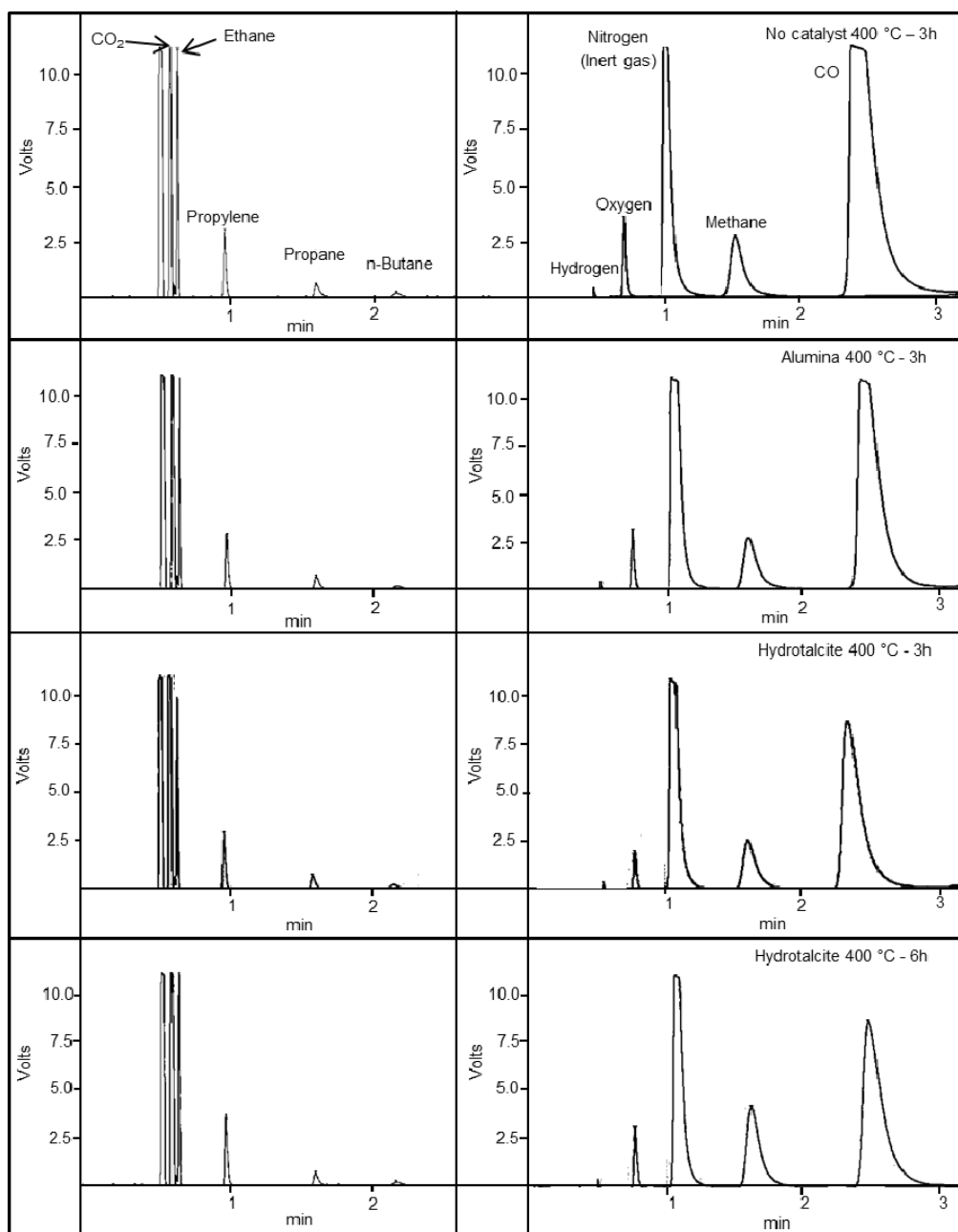


Figure 2: Principal compounds found in the gaseous products when tests were carried out at 400 °C

4. Conclusions

We studied the deoxygenation process through decarboxylation of the *Jatropha Curcas* oil. As result it was possible to obtain a liquid biofuel which is mainly composed of hydrocarbons, around 81 %, conformed as C8-C15 as prevailing fraction. The product showed significant improvement in terms of heating value, around 44 MJ/Kg, which is higher than that of biodiesel (39 MJ/Kg) and diesel (43 MJ/Kg), and viscosity (4 cSt), which is lower than that of biodiesel (4.5 cSt). The yields obtained for the overall process were greater than 80 %.

On the other hand using a GC analysis it was possible to identify the major compounds present in the gaseous products, confirming that the oxygen is removed mainly as CO₂ and CO. Other compounds such as methane, oxygen, hydrogen and light hydrocarbons were also identified.

5. Acknowledgments

The authors thanks Dr. A. Casazza, Dr. I. Di Termini and Prof. M. Rovatti from the Department of Civil, Chemical and Environmental Engineering (DICC) of the University of Genoa, for fruitful discussions.

References

- Chistyakov, A., Gubanov, M., Tsodikov, M., 2013. The direct conversion of rapeseed oil towards hydrocarbons over industrial catalysts. *Chemical Engineering Transactions*, 32, 1093-1098.
- Gillani, S., Belaud, J., Sablayrolles, C., Montrejeud-Vignoles, M., Le Lann, J., 2013. A CAPE based life cycle assessment for evaluating the environmental performance of non-food agro-processes. *Chemical Engineering Transactions*, 32, 211-216.
- Mäki-Arvela P., Kubičková I., Snåre M., Eränen K., Murzin D. Y., 2007, Catalytic deoxygenation of fatty acids and their derivatives, *Energy & Fuels*, 21, 30-40.
- Martins, M., Pires, R., Alves, M., Hori, C., Reis, M. Cardoso, V., 2013. Transesterification of soybean oil for biodiesel production using hydrotralcite as basic catalyst. *Chemical Engineering Transactions*, 32, 817-822.
- Morgan T., Grubb D., Santillan-Jimenez E., Crocker M., 2010, Conversion of triglycerides to hydrocarbons over supported metal catalysts, *Top Catal*, 53, 820-829.
- Morgan T., Santillan-Jimenez E., Harman-Ware A. E., Ji Y., Grubb D., Crocker M., 2012, Catalytic deoxygenation of triglycerides to hydrocarbons over supported nickel catalysts, *Chemical Engineering Journal*, 189, 346-355.
- Na J. G., Yi B. E., Kim J. N., Yi K. B., Park S. Y., Park J. H., Kim J. N., Ko C. H., 2010, Hydrocarbon production from decarboxylation of fatty acid without hydrogen, *Catalysis Today*, 156, 44-48.
- Na J.G., Han J.K., Oh Y. K., Park J. H., Jung T. S., Han S. S., Yoon H. C., Chung S.H., Kim J. N., Ko C. H., 2012, Decarboxylation of microalgal oil without hydrogen into hydrocarbon for the production of transportation fuel, *Catalysis Today*, 185, 313-317.
- Santillan-Jimenez E., Morgan T., Lacny J., Mohapatra S., Crocker M., 2013, Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel catalysts, *Fuel*, 103, 1010-1017.
- Snåre M., Kubičková I., Mäki-Arvela P., Eränen k., Murzin D. Y., 2006, Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel, *Industrial & Engineering Chemistry Research*, 45, 5708-5715.