**Answers to the Reviewers comments**

**Reviewer A**

The submitted paper present a extensive work on conventional catalyst synthesis, basic catalyst characterization and catalyst improvement in reaction of biodiesel synthesis with some superficial kinetic analysis. But, there are two main reasons for rejection of this paper for publishing in this journal:

1. The method of catalyst synthesis is already known (even published many times by authors too), the basic catalyst characterization do not show any deep analysis of catalyst structure corresponding to kinetic and catalyst application improvement. Additionally, the kinetic analysis on biodiesel synthesis is very basic without any literature research and connection on previous published data and not supporting the obtained results.

Authors´intention was not to present synthesis of MnCO3/Na-silicate as new method of catalyst preparation. The main goal was to prepare catalyst which is suitable for continuous process using packed-bed reactor.

Related to applied method of catalyst characterization, we had focused on conventional characterization methods of catalyst applied in the process of biodiesel synthesis in order to confirm catalyst structure, and to reveal whether any change occurred after the catalyst reutilization. The goal of the paper was not to present fine analysis of catalyst structure.

The part of the paper relating to kinetic analysis was supported by additional literature review where relation with previously published data can be seen (“Introduction” section, Page 3, lines 64-71, new References (27-34) were also added.

2. The length of paper is too long for research paper or short communication. From the other side, the subject and structure of paper do not have a review format to be published like that. So, by printing editing the paper will have 15-20 pages which is highly above required.

The manuscript has been shortened as suggested and prepared as “research paper”. Now it has 26 pages, including both abstracts (English and Serbian), Figures, Tables, Nomenclature and References.

Introduction section has been shortened significantly,and all other corrections made in order to satisfy the Reviewers suggestion are marked red in the manuscript.

3.Here, I would like to give some major comments for paper improvement and further explanation for rejection:

3.1 Why authors decided to research catalyst which could not be economically applied in industry? (by carefully research of published literature it could be concluded that such catalyst have some major obstacles for industrial application i.e. reusability and efficiency - this paper confirming that too, also temperature and time of reaction, type of reactor and so one...).

Among a very large number of scientific papers dealing with solid catalysts for biodiesel synthesis, almost neither is applied in industry. As far as we know, industrial biodiesel production using heterogeneous catalyst is still limited on Esterfip-H process developed by French Institute of Petroleum (IFP) and commercialized by Axens, which use mixed oxide of zinc and aluminium as catalyst and operate at high temperature and pressure. Although a great attention has been paid to the development of a catalytic material that will meet all requirements such as activity, stability and inexpensive preparation method, this task is still a challenge and need further intensive research.

The goal of our study was to obtain catalyst in the form of the granulesthat will be at the same time cheap, and with acceptable activity and stability, which would belater tested in the pilot plant for continuous transesterification process. MnCO3 appeared to be a good candidate, with the possibility to be used for 350h with satisfactory stability, butits powdered form (fine particles) is not suitable to be applied for continuous process.Thus the idea was to use MnCO3 in combination withsodium silicate water glass, which is known as a cheap adhesive, in order to obtain granulated particles. The results of this study revealed that the obtained MnCO3/Na silicate catalyst was sufficiently efficient and stabile with high FAME yield achieved after 9 cycles of repeated use.

3.2 Very poor literature review by every researched segment of paper: catalyst synthesis and characterization, process conditions and kinetic model.

More detailed literature review would have resulted in more pages, and even now the Reviewer’s comment was that the manuscript is too long.

Anyway, literature regarding kinetic models was added to Introduction section (see answer 1), and other segmentswere commented in “Results and Discussion” section using more references. For example:

In the Influence of temperature section:

-Page 7, lines 187-188: “…which is a consequence of the influence of Na-silicate, which possess activity even at lower temperature.18”

- Figure 1 was changed and comparison with results from ref. 8 was added.

-Page 7, lines 188-190:“Compared to MnCO3 catalyst where 2wt% was determined as optimal,8the yield of FAME could be additionally increased using higher amount of MnCO3/Na-silicate catalyst enabling the complete conversion of TAG followed with very high yield of FAME.”

Influence of methanol-to-oil molar ratio section: Page 13, line 292-294: “The same effect of methanol-to-oil molar ratio was obtained with MnCO3 catalyst used in the powder form, but FAME yield was increased only to 80% for methanol-to-oil ratio of 24:1.8”

Thermal analysis section, Page 16, line 344:“These results support previous findings related to temperature of MnCO3 decomposition.39”

X-ray diffraction section, Page 17, Line 359-361: “While MnCO3 in powder form undergone a slight change in structure after being reused8, this was not the case when MnCO3/Na-silicate was reused several times, showing that Na-silicate influenced positively its stability.”

3.3The most important: I could not see the difference between the catalyst efficiency, the MnCO3/Na-silicate investigated in this paper and MnCO3 investigated in authors' previous works? It could be that there is no synergetic effects of support and active phase since the amount of catalyst is not the same and amount of used methanol too. Authors, should give more detailed comparison easily understandable for all readers.

The difference between MnCO3/Na-silicate investigated in this paper and MnCO3 investigated in our previous work can be primarily seen in the transesterification of soybean oil at lower temperature. In the case of MnCO3 (ref 8 in the manuscript), it was determined that 2wt% is the optimum catalyst amount and the further increase did not affect the TAG conversion and FAME yield, implying that amount of 5wt% (which was used in experiments with MnCO3/Na-silicate) would not have affected the obtained results.

The main role of the Na/silicate was to act as an (cheap) adhesive that will enable production of thegranulated catalyst with desired strength and size, which could not be successfully accomplished with pure MnCO3. In Introduction section (Page 2, lines49-51) is also stated that there was a problem when MnCO3 in powder form was used in a packed-bed reactor, stressing the necessity of converting powder catalyst to granulated one. Thus, the main goal of this study was to prepare granulated catalyst, comparedto MnCO3, which is inpowder form(previous work), test it under different reaction conditions, characterize both fresh and used catalyst and analyze the experimental data to define kinetic model which might be later used for designing of larger size tubular reactor packed with MnCO3/Na-silicate as catalyst.

The comparison with MnCO3catalyst was amplified and explained in more details (Page 7, lines 181-190; Page 8, lines198-200; Page 13, lines 292-296; Page14, lines 307-310; Page 13, lines 323-324, Page17, lines 359-361), and even the Fig.1 was modified whereinTAG conversion and FAME yield at different temperature when MnCO3 was used was added in order to make the difference at low temperature clearer.

3.4 Moreover, page 8, lines 206-207: "determined TAG conversion was only about 20% at 392 K, MnCO3/Na-silicate showed much higher activity with 24.6% of TAG..." difference of 4.6% for such reaction is not much higher, it is minor difference. Please, change that.

The Reviewer did not read the sentence carefully;the conversion of 24.6% was obtained at 333K, obviously lower temperature, and at 388K the conversion was 68.2%. The difference between 20% and 68.2% could not be considered as minor; it is over 3 time higher conversion.

The sentence has been rewritten in order to be clearer, and only FAME yield at similar temperature are compared now (Pages 7, lines 185-187).

3.5 Also, influence of each parameters (temperature, oil to methanol molar ratio, time of reaction, number of repetition) could not be compared at all since all other parameters are not constant. Namely, influence of temperature, time of reaction is examined for 18:1 molar ratio and 5% catalyst and effect of repeated use for 30:1 and 10% catalyst.

Influence of temperature and reaction time were tested at 18:1 molar ratio, and after that molar ratio of methanol to oil was optimized, showing that 30:1 gave better results. This is the reason why reaction conditions are different in repeated use of catalyst. The same case was with catalyst amount, after optimization it was found that 10wt% gives best results, thus it was further used in repeated use of catalyst. The new Section named “Influence of catalyst amount” has been added, Page 14 and also as Fig. 5, and from these results could be seen why 10% was further used in the tests of catalyst reusability.

3.6 Regarding kinetics, all your results indicate and confirming conclusion in literature that increasing amount of catalyst, or temperature, or amount of oil will not result in required FAME yield (even you didn't conclude that but could be easily visible). The reason is complexity of kinetics for this reaction. The reversible steps and different thermodynamic phase in reactor highly determined the products. So, literature research about kinetics in such system should be better analyzed and new process parameters should be chosen for investigation.

Literature review regarding kinetics has been added to Introduction sectionof the manuscript (see answer to 1). Different approaches to analysis of kinetics data are reported in literature, from the most frequently used first order, to more complex models which include Eley-Rideal or Langmuir-Hinshelwood reaction mechanism, or consisting of three and four consecutive and reversible reactions.Although kinetic studies of 3-step transesterification reaction have beenreported several times, this approach is complex, time consuming and needs computer programs for calculations and more experimental data for parameters determination therefor if it is possible should be replaced by simple kinetic models.

In the present study the reversible reactionwas neglected since the excess of methanol was used. Based on the literature survey, we have found that three models are the most proper to be used for describing the kinetics of transesterification of soybean oil using MnCO3/Na-silicate catalyst. Two of them (IL and MM model) have been confirmed as models that well describe kinetics of heterogeneously catalyzed process both at lower (60 °C) and higher temperatures, and for a large variety of solid catalysts (ref.8,25,26,33,34,35). IL model comprises both the triglycerides mass transfer and chemical reaction controlled regimeand is based on the Eley–Rideal mechanism, while MM model involves the changing mechanism of the reaction and the TAG mass transfer limitation, thus both of them not being so simple.

3.7 In part titled: Leaching of Na and Mn in biodiesel and glycerol, based on data shown in figure 10 and other data described in experimental part, it could be easily calculated that after 9 reuse of the same catalyst the 1.65% of Mn is leached from the catalyst and 192.5% of Na. Could you please explain this? This is also confirming my doubt about difference between MnCO3/Na-silicate investigated in this paper and MnCO3 investigated in authors' previous works, since if all Na is leached from the reaction mixture after the first two uses there is no its catalytic influence (the TAG conversion remain). Could you explain this too? Or you just have wrong data in your paper.

The Reviewer calculation is not quite clear. If 1kg of oil was used in transesterification, about 1kg of FAME (slightly less i.e. 915g) and only about 104 g of glycerol will be produced if conversion is 100%. The amount of Na that is leached from the catalyst after 9 cycles, starting from 1 kg of oil and calculating using the obtained values of FAME yield from Fig 6 for each cycle would be 3795 mg in FAME and 973 mg in glycerol phase, which is 4768 mg total. The mass of the catalyst used will be 100 g (10% based on oil, and the mass of oil is 1000 g). If we know that mass ratio of Na-silicateto MnCO3was 0.9:1, this means that the catalyst contain 47.4 g of Na silicate and 52.6 g of MnCO3. The mass of Na in 47.4 g ofNa2O·*3.3*SiO2 is 8.37g. Thus, since the leached amount of Na in both phases is 4.768 g, it means that 56.97% Na from catalyst was dissolved after 9 cycles.

Although some amount of Na ion is obviously leached from the catalyst, certain amount of Na still remained probably in the internal part of the catalyst particle. From the XRD of used catalysts (both MnCO3/Na-silicate and MnCO3 [ref 8]) could be seen that while MnCO3 after being reused undergone a slight change in structure, this was not the case when MnCO3/Na-silicate was reused several times. Obviously, the presence of Na-silicate influenced positively catalyst stability. The main difference between MnCO3/Na-silicate and MnCO3 is the form of the catalyst, and other is that the presence of Na-silicate contributed to the catalyst activity at lower temperature.

Reviewer D

Original scientific paper and no corrections are required. Serious and nice paper, correctly written. It deserved to be published as is prepared.

Answer to Reviewer D:

Thank you for such nice opinion.

Reviewer E

The manuscript entitled ″**Biodiesel synthesis and kinetic analysis based on MnCO3/Na-silicate as heterogeneous catalyst″** represents a comprehensive study on the utilization of a heterogeneous catalyst for biodiesel synthesis in the form of solid particles prepared from Na-silicate and Mn-carbonate. Beside the catalyst preparation and characterization, the study encompasses the optimization of the parameters of the catalyzed biodiesel synthesis on soybean oil, analysis of the reaction kinetics as well as the catalyst stability (reusability) assessment. The manuscript is interesting and valuable for development of new heterogeneous catalysts.

However, the following specific points should be addressed in this manuscript:

**Page 4-Catalyst preparation.**

1. The catalyst preparation, which is an important part of the study objective, was not defined thoroughly. The procedure should be more precise described regarding hydration (the amount of water), type of rotary granulator and more procedure details should be given.

The procedure of catalyst preparation is given with more details (Page 4) and citation (ref 36).

2. Also, the following sentence is not clear enough.

″For comparison, two complexes, named Na complex, and Mn complex, using only hydrated sodium silicate and manganese carbonate, respectively, were also dried at 333 K for 24 h and then grinded to fine powder″.

Please, explain what kind of comparison? Specify in which experiments was the comparison done. Why are named complexes?

The sentence was rephrased since the word “complex” had not been appropriately used. It refers to two starting materials for catalyst preparation, namely, Na-silicate (hydrated sodium silicate) and MnCO3. They were also subjected to characterization in order to obtain better insight of the structure of the prepared catalyst compared to the starting material.

Now, Page 4, line 101-102: “For comparison, starting materials, Na-silicate and MnCO3, were also dried at 333 K for 24 h, grinded and subjected to characterization.”

3.The statistic methods used to evaluate the experimental results should be described in Experimental section rather than in the footnote of the Table 1 (line 282-283, p 13).

The Mean Relative Percent Deviation (MRPD) calculation was transferred from the footnote of the Table 1 to Experimental section (Page 5, line 133-135): ‘The significance of the kinetic model was statistically evaluated using the mean relative percent deviation (MRPD) between the calculated and experimentally determined TAG conversion degree according to the equation:

 (5)

4.**Page.7- Results and discussion**

The methods used in optimization of catalyst preparation (line 179-182) should be described in Experimental section.

The sentence regarding the optimization of catalyst preparation was added to Experimental section (Page 4, line 96-98).

5.Page 8 line 207: Is the term ′much higher activity′ adequate in this case?

This was changed and the sentence rewritten in order to be more clear and precise (given as the answer to Reviewer A 3.5).

6.Although the models designated with abbreviations MM an IL were adopted from the literature, the full name of the terms which are abbreviated should be given at the place of the first abbreviation appearance.

This was corrected andabbreviation is given at the place where the used models first appeared (Page 3, line 80-83).

7.The effect of catalyst concentration was not shown and explained. Namely, the authors are using 5% of the catalyst in many presented experiments, however later on they utilized 10% of the catalyst, and obtained the highest product yield. This should be explained and justified.

The effect of catalyst amount on TAG conversion and FAME yield is added as a new Section (Page 14) and also as Fig. 5, and from these results could be seen why 10% was further used in the tests of catalyst reusability.