



Heterogeneous synthesis of biodiesel: comparison of alkaline catalysts supported by biochar



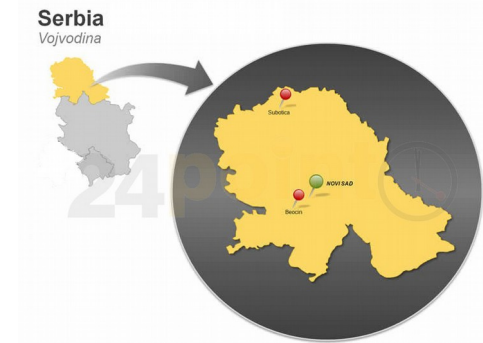
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There are two specific project tasks:

- to characterize biochar samples produced under different pyrolytic conditions, including various biomass-based feedstocks (poster no. 56) and
- **to explore the efficiency of catalysts developed using the selected biochar in biodiesel synthesis, with the first results reported in this presentation.**

Biodiesel
(chemically=fatty acid alkyl (mostly methyl) esters)
is biofuel
produced from vegetable, animal or algal-based
triglycerides.

It is **alternative** for fossil diesel fuel, having main advantages of being **renewable and biodegradable fuel**, **not containing sulphur and aromatic compounds**, and **having oxygen in the molecule**, all that leading to **less harmful emission of pollutants** and **less negative effects to the global carbon cycle.**



Currently, biodiesel production is based on **homogeneous alkaline transesterification** using base catalysts like KOH, NaOH or C_2H_5ONa .

However, such production is **linked to extensive washing** of biodiesel and glycerol (which is a by-product in transesterification reaction) in order to remove liquid catalysts, **producing large quantities of wastewater**.

This is one of the main reasons behind **strong motivation** for developing high-performance heterogeneous **SOLID CATALYSTS** as their use in transesterification is a way of omitting the washing of the product(s).

Moreover, the solid catalyst can be easily removed from the liquid products and it can be re-used in several cycles.

Different heterogeneous catalysts have been tested for biodiesel production:

- **alkali or alkaline earth oxides,**
- **supported alkali metals and**
 - **basic zeolites,**

but only a few of them can be used on industrial scale owing to the **high synthesis cost.**

- **The next step towards the intensification of biodiesel production is to use waste materials as feedstock for the synthesis of cost-effective catalyst.**

Among the **heterogeneous catalysts**,
those based on biochar support have been attracting increasing
attention.

Biochar is a carbon-rich, porous residue, which can be formed **by thermal decomposition of various types of feedstock like different low cost lignocellulosic wastes often locally available** in a reactor without presence of air and at moderate temperatures
- **slow pyrolysis or hydrothermal carbonization/liquefaction.**

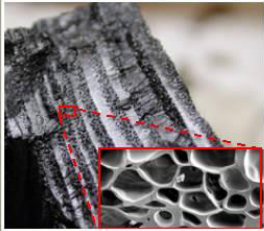


MATERIALS AND METHODS

Biochar used in this work was supplied by **Basna d.o.o. Company** from **Čačak** and it **was obtained by slow pyrolysis of beech at 700°C and 800°C** (denoted as B-BC-700 and B-BC-800, respectively).

All samples were dried overnight at 120°C and sieved to obtain particles of size <500 µm.

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- Biochar-based catalysts for biodiesel synthesis were prepared *via* different preparation methods: wet impregnation and ball milling.
- K_2CO_3 and CaO were used as active phases with 30 wt% loading (relative to biochar mass).

| Catalyst preparation | Catalyst sample code |
|--|----------------------|
| 30 % (m/m) K_2CO_3 on B-BC-800 – wet impregnation with K_2CO_3 , dried at 120°C for 24 h and calcined in N_2 at 700°C - 3h | CAT_A |
| 30 % (m/m) K_2CO_3 on B-BC-700 – wet impregnation with K_2CO_3 , dried at 120°C for 24 h and calcined in N_2 at 700°C - 3h | CAT_B |
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with CaO, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_C |
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with $Ca(CH_3COO)_2 \cdot xH_2O$ as precursor of active phase, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_D |
| 3 % (m/m) K_2CO_3 , 27 % (m/m) CaO on B-BC-800 – wet impregnation with K_2CO_3 and CaO, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_E |
| 30 % (m/m) CaO on B-BC-800 – ball-milling with CaO, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_F |
| 3 mas% K_2CO_3 , 27 mas% CaO on B-BC-800 – ball-milling with K_2CO_3 and CaO K_2CO_3 and CaO, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_G |

In this way, use of these 7 catalysts in transesterification reaction enabled comparison of their efficiencies taking into account:

- **two biochar supports obtained by slow pyrolysis of beech at two temperatures (700°C and 800°C),**
 - **two active catalytic phases, K_2CO_3 and CaO,**
 - **two methods of catalyst preparation, and even**
- **different precursors of the active phase (in the case of CaO: commercial CaO, $Ca(CH_3COO)_2 \cdot xH_2O$, or CaO doped with K_2CO_3)**

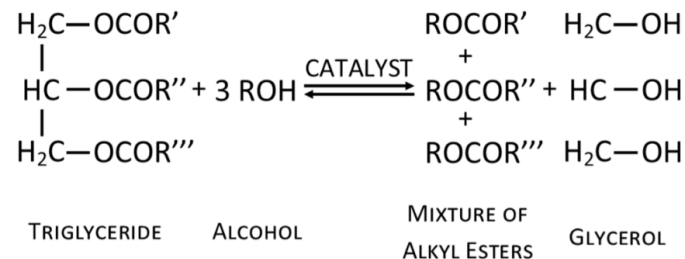
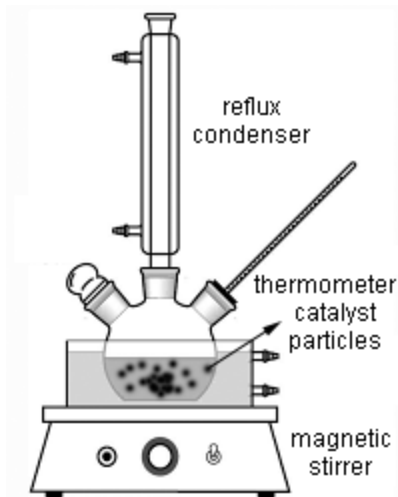
All synthesized catalysts were characterized by different methods:

- **SEM with EDX,**
 - **XRD,**
 - **BET,**
 - **FTIR and**
- **TPD (CO₂) methods**

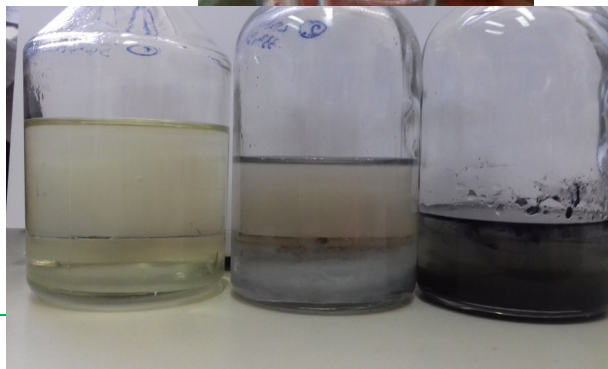
in order to correlate the properties like morphology, cristallinity, pore size distribution, specific area, etc., with the obtained efficiency in synthesis of biodiesel.

Transesterification – synthesis of biodiesel (fatty acid methyl esters-FAMES)

- sunflower, refined edible oil, 150 g
- methanolysis (8:1 MeOH:oil)
- biochar-supported catalyst, 4% (m/m) relative to oil
- reaction temperature 60°C
- the reaction time was 2 h
- the reaction mixture was placed in a separatory funnel overnight for separation of phases



- it was observed that if the reaction was successful, the phase separation easily occurred and after the recovery of the upper layer of esters, the remaining methanol was evaporated under vacuum, and then analyzed by GC-FID without any further purification
- if the reaction was not completed, the catalyst remained in the upper phase, and clear separation was not observed, thus recovery of the upper phase was very hard and incomplete and this was the reason why yield was not measured at this phase of the study.



GC analysis

- **determination of purity of the upper esters' phase with respect to the presence of 6 fatty acid methyl esters (C16:0, C18:0, C18:1, C18:2, C18:3, C20:0), which served as a measure of the catalyst efficiency in the transesterification reaction**
- a gas chromatograph GC-2010 plus, Shimadzu, equipped with a capillary column InterCap (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) and flame-ionization detector.
- standard mixture of methyl esters RM-1
- methyl heptadecanoate (purity > 99%) as an internal standard

| Item | Description/Condition |
|---------------------------|-----------------------------------|
| Column flow | 0.54 mL \cdot min ⁻¹ |
| Split ratio | 40:1 |
| Sample volume | 1 μL |
| Oven Program Initial Temp | 200 °C |
| Hold time 1 | 5 min |
| Rate 1 | 4°C \cdot min ⁻¹ |
| Oven Program Final Temp | 240 °C |
| Hold time 2 | 5 min |
| Equilibration Time | 1 min |
| Carrier Gas | Helium |
| Gas flow | 3 mL \cdot min ⁻¹ |
| FID temperatures | 260 °C |
| H ₂ Flow | 40 mL \cdot min ⁻¹ |
| Air Flow | 400 mL \cdot min ⁻¹ |
| Makeup Flow | 30 mL \cdot min ⁻¹ |

All the experiments were done in duplicate and the average values were calculated.

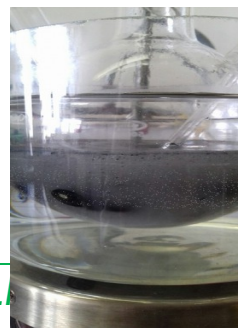
RESULTS

| Catalyst preparation | Catalyst sample code | Purity of the esters layer, % | Purity of the esters layer, %, after the re-use of the catalyst |
|---|----------------------|-------------------------------|--|
| 30 % (m/m) K_2CO_3 on B-BC-800 – wet impregnation with K_2CO_3 , dried at 120°C for 24 h and calcined in N_2 at 700°C - 3h | CAT_A | 99.8 (92.3 tablets) | 3.1 |
| 30 % (m/m) K_2CO_3 on B-BC-700 – wet impregnation with K_2CO_3 , dried at 120°C for 24 h and calcined in N_2 at 700°C - 3h | CAT_B | 85.1 | |
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with CaO , dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_C | 76.5 | 23.9 |
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with $Ca(CH_3COO)_2 \cdot xH_2O$ as precursor of active phase, dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_D | 29.8 | |
| 3 % (m/m) K_2CO_3 , 27 % (m/m) CaO on B-BC-800 – wet impregnation with K_2CO_3 and CaO , dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_E | 68.7 | |
| 30 % (m/m) CaO on B-BC-800 – ball-milling with CaO , dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_F | 19.6 | |
| 3 mas% K_2CO_3 , 27 mas% CaO on B-BC-800 – ball-milling with K_2CO_3 and CaO K_2CO_3 and CaO , dried at 120°C for 24 hand calcined in N_2 at 700°C - 3h | CAT_G | 76.7 | |
| biochar “as produced” B-BC-800 | | 3% | |

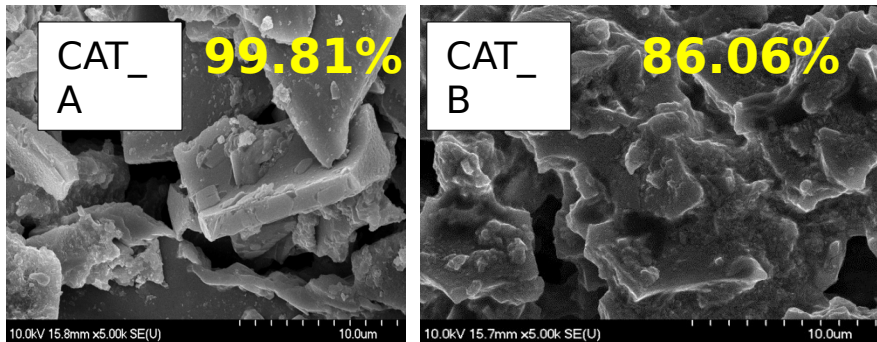
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| 30 % (m/m) K_2CO_3 on B-BC-700 – wet impregnation with K_2CO_3 , dried at 120°C for 24 h and calcined in N_2 at 700°C - 3h | CAT_B | 85.1 | |

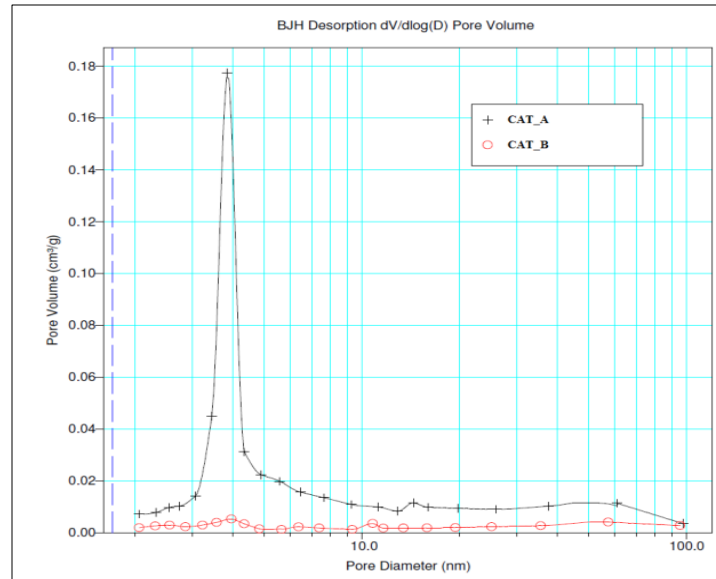
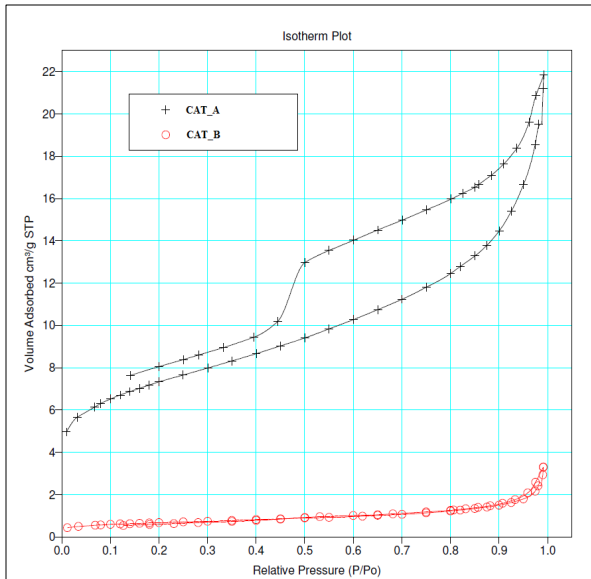
- the highest measured purity of esters layer was obtained for both cases of using K_2CO_3 -biochar catalyst, with the higher value obtained for biochar support produced at the higher pyrolysis temperature
- however, reuse of this catalyst was not successful probably due to leaching of the active phase
- tableting of the catalyst under high pressure was performed (presuming that tablets could make easier catalyst removal) but unsuccessfully, because tablets were suspended under stirring conditions



K₂CO₃ – based catalysts:



CAT_A and CAT_B are morphologically different, but have the similar composition of **active phase - K₂CO₃ and K₂O** – confirmed by XRD.



The higher activity of CAT_A can be associated with its beneficial textural properties mainly originated from the used biochar as a support (higher BET and total pore volume).

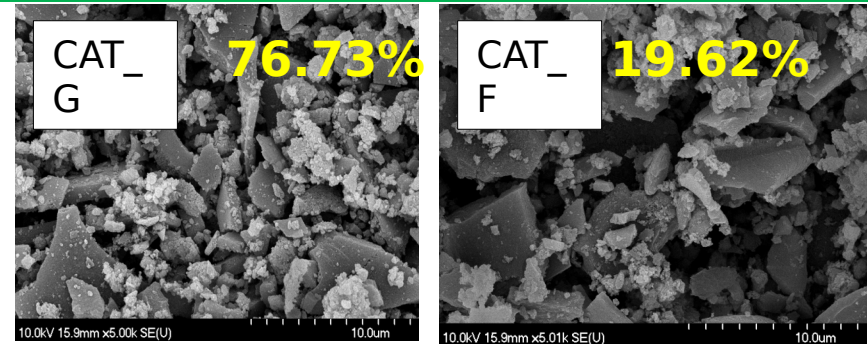
RESULTS

| Catalyst preparation | Catalyst sample code | Purity of the esters layer, % | Purity of the esters layer, %, after the re-use of the catalyst |
|--|----------------------|-------------------------------|---|
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with CaO, dried at 120°C for 24 hand calcined in N ₂ at 700°C - 3h | CAT_C | 76.5 | 23.9 |
| 30 % (m/m) CaO on B-BC-800 – wet impregnation with Ca(CH ₃ COO) ₂ ·xH ₂ O as precursor of active phase, dried at 120°C for 24 hand calcined in N ₂ at 700°C - 3h | CAT_D | 29.8 | |
| 3 % (m/m) K ₂ CO ₃ , 27 % (m/m) CaO on B-BC-800 – wet impregnation with K ₂ CO ₃ and CaO, dried at 120°C for 24 hand calcined in N ₂ at 700°C - 3h | CAT_E | 68.7 | |
| 30 % (m/m) CaO on B-BC-800 – ball-milling with CaO, dried at 120°C for 24 hand calcined in N ₂ at 700°C - 3h | CAT_F | 19.6 | |
| 3 mas% K ₂ CO ₃ , 27 mas% CaO on B-BC-800 – ball-milling with K ₂ CO ₃ and CaO K ₂ CO ₃ and CaO, dried at 120°C for 24 hand calcined in N ₂ at 700°C - 3h | CAT_G | 76.7 | |

- CaO-based catalysts showed wide range of efficiencies in term of the esters purity, with the highest values between 69-77% obtained for CAT_C, _E, and _G.
- Use of Ca-acetate/wet impregnation and commercial CaO/ball-milling seemed to be unsuccessful for the biochar/based catalyst preparation, while on other hand wet impregnation was more efficient in the case of commercial CaO, and both methods of catalyst preparation – wet impregnation and ball milling gave similar results for CaO doped with K₂CO₃

CaO – based catalysts:

- The active phase and the biochar support can be clearly differentiated.
- The biochar particles in all samples have irregular shapes and rough edges, wherein their size is reduced after the ball-milling treatment.
- Active phase in all catalysts is present in the form of irregular aggregates of numerous nanoparticles and the aggregation tendency is favored by the wet impregnation catalyst synthesis route.



Similar morphological and textural properties indicated that they originated from the biochar as a support.

| Catalyst sample | BET (m ² /g) | Average pore diameter (nm) | Total pore volume (cm ³ /g) |
|-----------------|-------------------------|----------------------------|--|
| CAT_C | 222.7 | 5.3 | 0.17 |
| CAT_D | 229.8 | 5.7 | 0.17 |
| CAT_E | 206.0 | 5.1 | 0.17 |
| CAT_F | 243.8 | 5.7 | 0.18 |
| CAT_G | 168.0 | 5.5 | 0.16 |

- Concerning the specific area and porosity parameters, there were no marked differences between CaO-based catalysts.
- Very small mesopores (close to micropores) are present in all CaO-based catalyst samples and the achieved efficiencies in terms of esters' layer purity is not related to the specific surface area, indicating that the reaction mainly takes place at the external catalyst surface.

Active phase composition of CaO – based catalysts by XRD analysis:

| Catalyst sample | Active phase composition | Crystallite size (nm) | Quatification (wt%) – active phase only |
|-----------------|--------------------------|-----------------------|---|
| CAT_C | Ca(OH) ₂ | 10.6 | 100.0 |
| CAT_D | Ca(OH) ₂ | 10.7 | 69.0 |
| | CaO | 44.1 | 4.0 |
| | CaCO ₃ | 21.0 | 27.0 |
| CAT_E | Ca(OH) ₂ | 11.3 | 75.2 |
| | CaO | 41.9 | 4.0 |
| | CaCO ₃ | 20.0 | 20.8 |
| CAT_F | Ca(OH) ₂ | 11.2 | 65.7 |
| | CaO | 31.0 | 15.2 |
| | CaCO ₃ | 17.4 | 19.2 |
| CAT_G | Ca(OH) ₂ | 11.5 | 82.8 |
| | CaO | 41.9 | 5.1 |
| | CaCO ₃ | 37.3 | 12.1 |

- ❖ The purity of the esters phase seemed to be depended on the catalyst active phase composition – the highest purity in the case of CaO-based catalysts was obtained with those having the higher content of portlandite (Ca(OH)₂).

GENERAL CONCLUSION AND PLAN FOR FURTHER INVESTIGATION:

Biochar-supported K_2CO_3 catalyst seems to represent more efficient and viable option for heterogeneous transesterification than CaO-catalysts, but further work has been planned in order to study:

- **leaching of K_2CO_3 , in order to provide the standardized quality of biodiesel in terms of maximum allowable content of K, and also to enable**
 - **the efficient reuse of the prepared catalyst, taking also into account methods for easier removal of catalyst from the reaction mixture, and finally to**
- **investigate synthesis of biodiesel under different reaction conditions in order to optimize the heterogeneous production, including also application of low quality raw materials.**



Thank you for your kind attention!

Heterogeneous synthesis of biodiesel: comparison of alkaline catalysts supported by pyrolytic biochar

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Tabela 3. Elementarni sastav uzoraka biougolja

| <i>Oznaka uzorka biougolja</i> | <i>C (mas%)</i> | <i>O (mas%)</i> | <i>Mg (mas%)</i> | <i>Si (mas%)</i> | <i>K (mas%)</i> | <i>Ca (mas%)</i> | <i>Na (mas%)</i> | <i>Al (mas%)</i> | <i>P (mas%)</i> | <i>Fe (mas%)</i> | <i>Cl (mas%)</i> | <i>Br (mas%)</i> | <i>S (mas%)</i> |
|--------------------------------|-----------------|-----------------|------------------|------------------|-----------------|------------------|------------------|------------------|-----------------|------------------|------------------|------------------|-----------------|
| WS-BC-700* | 74,61 | 15,42 | 0,39 | 6,98 | 1,01 | 1,58 | - | - | - | - | - | - | - |
| WS-BC-700** | 78,82 | 15,26 | 0,34 | 3,88 | 0,64 | 0,91 | - | - | 0,15 | - | - | - | - |
| BSG-BC-700* | 70,23 | 19,31 | 0,24 | 8,58 | - | 0,47 | 0,30 | 0,20 | 0,65 | - | - | - | - |
| BSG-BC-700** | 81,05 | 9,26 | 0,62 | 2,49 | - | 2,54 | 0,44 | 0,18 | 3,06 | 0,36 | - | - | - |
| SS-BC-700* | 68,64 | 15,33 | 1,65 | 0,52 | 1,11 | 11,94 | - | 0,32 | - | - | 0,50 | - | - |
| SS-BC-700** | 71,15 | 15,62 | 1,97 | 0,39 | 4,68 | 5,39 | - | 0,26 | - | - | 0,29 | - | 0,24 |
| C-BC-700* | 82,09 | 16,66 | - | 0,12 | 0,76 | - | - | 0,08 | 0,22 | - | - | - | - |
| C-BC-700** | 82,83 | 11,75 | - | - | 3,47 | - | - | 0,20 | 0,15 | - | 1,60 | - | - |
| B-BC-700* | 89,67 | 9,43 | - | - | 0,45 | 0,45 | - | - | - | - | - | - | - |
| B-BC-700** | 85,89 | 12,96 | - | - | 0,63 | 0,35 | - | - | - | - | 0,17 | - | - |
| B-BC-800* | 84,33 | 7,23 | - | - | 3,62 | 4,49 | - | - | - | - | - | - | - |
| B-BC-800** | 89,31 | 9,92 | - | - | 0,16 | 0,52 | - | - | 0,10 | - | - | - | - |
| B/O-BC-700* | 87,25 | 10,85 | - | - | 0,87 | 0,90 | - | 0,13 | - | - | - | - | - |
| B/O-BC-700** | 88,16 | 10,60 | - | - | 0,56 | 0,45 | - | - | - | - | - | 0,51 | - |

*1. pozicija merenja; **2. pozicija merenja