

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

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Biodiesel is commercialized biofuel with significant quantities produces all over the world, particularly in the EU. It is alternative for fossil diesel fuel, having main advantages of being renewable and biodegradable fuel, not containing sulphur and aromatic compounds, leading to less harmful emission of pollutants and less negative effects to the global carbon cycle (Đurišić-Mladenović *et al.*, 2018). Currently, its production is based on homogeneous alkaline transesterification. 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.

Among the heterogeneous catalysts, those based on biochar-supported alkaline or acid catalysts for biodiesel production have been attracting increasing attention, particularly taking into account that their precursors are low cost feedstock like various lignocellulosic waste locally available (Niu *et al.*, 2018; Sano *et al.*, 2017; Shankar *et al.*, 2017). Biochar is defined as a carbon-rich, porous solid produced by thermal decomposition of biomass in a reactor with little or no available air and at moderate temperatures (Liu *et al.*, 2015).

The aim of a project “Contribution to the sustainable development of AP Vojvodina through the utilization of waste biomass towards biofuel production” funded by Secretariat for High Education and Science of Autonomous Province of Vojvodina, Republic of Serbia, is to investigate heterogeneous catalysts for biodiesel synthesis based on biochar produced by pyrolysis of lignocellulosic materials largely available in Serbia. In fact, there are two-fold goal of the project: firstly, to characterize biochar samples produced under different pyrolytic conditions and secondly, to explore their efficiency in biodiesel synthesis.

This study reports preliminary results obtained for different alkaline biochar-based catalysts applied in transesterification reaction. Only results obtained for samples of woody-based biochar were reported here, even though biochar from agricultural waste is also covered by the project. Biochar was wet impregnated; K₂CO₃ and CaO were used as active phases with 30 wt% loading. The obtained suspension were evaporated under vacuum, dried at 120°C for 24 h and calcinated in N₂ flow at 700°C for 3 h. In order to check intrinsic catalytic activity of catalyst support itself, sample of as-synthesized biochar was also tested in transesterification reaction.

The sunflower oil purchased as edible oil from a supermarket was used taking into account that this kind of refined oils is the best feedstock for biodiesel sythesis not introducing problems caused by poor quality feedstock into this first phase of new catalyst development. A three-neck flask mounted with a condenser was used as a batch reactor. The usual methanol to oil molar ratio of 8:1 is used for the synthesis; surplus of methanol (above the stoichiometric quantity equal to molar ratio of 3:1) forces the reversable reaction of transesterification towards the products formation. The amount of catalyst added to the oil was equal to 4 wt%. Transesterification was performed at 64°C for 2 hours. Afterwards, the reaction mixture was transferred to a separatory funnel and left for phase separation. The upper layer of biodiesel was removed by pipette and analyzed by gas chromatography with flame ionization detector (GC-2010 plus, Shimadzu) in order to obtain the content of fatty acid methyl esters and in this way to compare the efficiency of different catalysts. Operational conditions for gas chromatographic analysis of biodiesel could be found elsewhere (Tomić *et al.*, 2019). The lower layer of glycerol and settled catalyst was further separated and the recovered catalyst was used to study its reusability.

Figure 1 illustrates the first biodiesel samples synthesized by using two produced catalysts (K₂CO₃ and CaO) supported by beech biochar. Difference in their activity is easily visible (Figure 1). The upper layer obtained in transesterification with K₂CO₃-based biochar was clear and quickly separated from catalyst-glycerol phase, while the phase separation after transesterification in the presence of CaO-based biochar was more difficult and the biodiesel layer contained soap-like sediment. The GC analysis revealed that K₂CO₃-biochar catalyst led to biodiesel containing 99.81% fatty acid methyl esters, which is above the minimum of 96.5% esters required by the EN14214 standard for quality of biodiesel to be used in diesel engine. The CaO-biochar catalyst led to synthesis of biodiesel with 76.53% of methyl esters, not complying the relevant request of EN14214. In other words, CaO-based catalyst was less efficient under the same reaction conditions than K₂CO₃-catalyst.

Transesterification in the presence of as-synthesized biochar was not efficient at all, suggesting the absence of alkaline active sites on biochar surface.

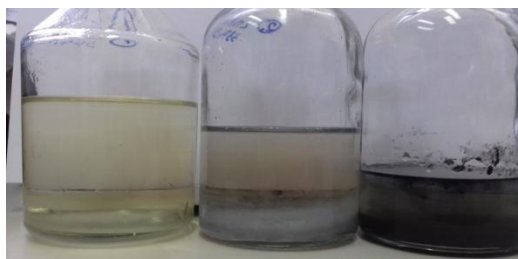


Figure 1. The upper layer separated from the reaction mixture after 2 h transesterification with different solid phases (from left to right): K₂CO₃-based biochar, CaO-based biochar and biochar

It is expected to obtain more results from on-going experiments using K₂CO₃- and CaO-based catalyst supported with biochar produced by pyrolysis performed under different conditions, thus having different structural, morphological and textural properties. The correlation between the biochar properties and the catalyst efficiency measured by the ester content in the synthesized biodiesel will be evaluated. For catalysts with the highest efficiency, optimization of transesterification parameters like methanol to oil molar ratio, catalyst to oil mass percentage and reaction time will be performed.

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