10th International Conference
Fuel Science – From Production to Propulsion

May 10 to 12, 2022

Cluster of Excellence
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CONFERENCE REPORT

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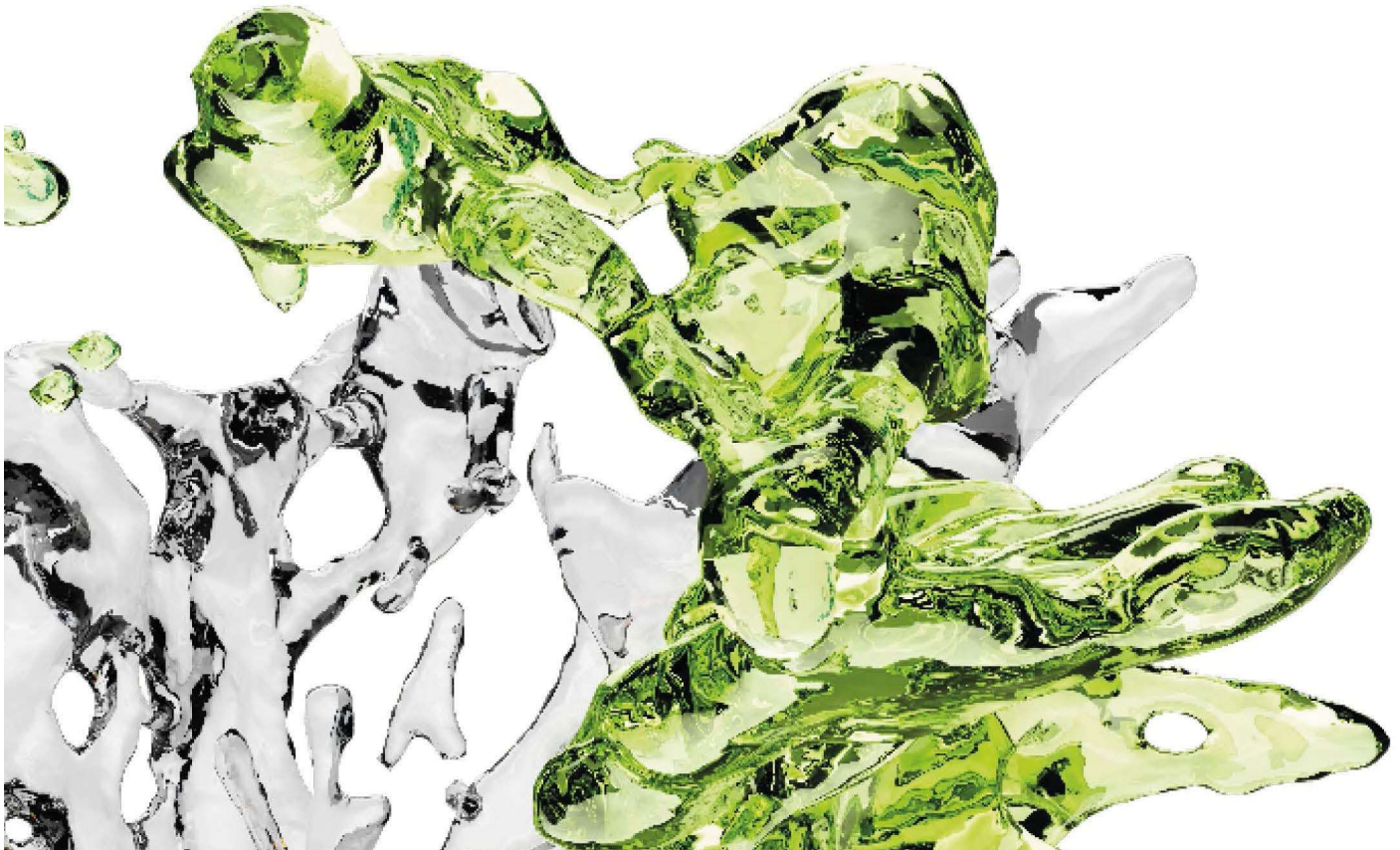
Fuel Synthesis II



Acceleration of biodiesel production from off-grade oil over waste-based CaO catalyst

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Abstract
Waste-based CaO was synthesized from chicken eggshell, which calcined form (900 °C, 5 °C/min, 4 h) was hydrated (80 °C, S:L=1:5, 24 h) and rehydrated/calcined (600 °C, 5 °C/min, 4 h). The obtained catalyst was characterized (Hg-porosimetry and TPD-CO_2) and tested in biodiesel synthesis from off-grade sunflower oil by transesterification to analyse the influence of water addition on reaction intensification. Water content was varied in the range from 1 wt% to 9 wt% by weight of oil. It is shown that water addition positively affects the catalytic activity leading to a reduction in induction time and to faster achievement of the reaction equilibrium (fatty acid methyl esters content > 95%), which for a water content higher than 1 wt% is achieved in 90 min. On the other hand, the equilibrium for the reaction without water addition was achieved considerably later (after 150 min).

Key words
green catalysts, waste utilization, transesterification, reaction intensification, energy,

Introduction

The chemical composition of feedstocks for biodiesel production is often unfavourable for catalysts, especially due to the presence of free fatty acids and water content [1]. In the case of base-catalyzed processes, free fatty acids lead to saponification reaction and deactivation of catalyst [2]. However, the addition of water can have a positive effect because it directly affects the reaction mechanism and can determine the course of the reaction, esspecially in the introductory part of the reaction where mass transfer resistance is dominant [3].

Methodology

CaO was derived from waste chicken eggshell calcined at 900 °C (heating rate of 5 °C, 4 h). The catalyst (ES-600HD) was synthesized in hydration (80 °C, S:L=1:5, 24 h) and dehydration (600 °C, 5 °C/min, 4 h) processes. The obtained catalyst was tested in transesterification reaction (temperature of 60 °C, methanol to oil molar ratio of 12:1, and catalyst concentration of 4 wt%). The analysed water contents were 1, 3, 5, 7, and 9 wt% by weight of oil. The reaction process was monitored by HPLC. The porosity parameters were determined by Hg-intrusion porosimetry, whereas base centre ranges and basicity were determined by TPD-CO_2.

Results and Discussion

The successfully synthesized catalyst exhibits the developed structure of pores and pore networks with an average pore diameter centred about 650 nm and porosity of 46.7%, indicating a macroporous structure suitable for undisturbed diffusion of large organic molecules, such as triacylglycerols (TAGs). TPD-CO_2 profile (Fig. 1) indicates the presence of medium (300-600 °C) and strong (>600 °C) active basic sites dispersed over moderately developed surface area (17.9 m^2/g) available for adsorption of reaction species.

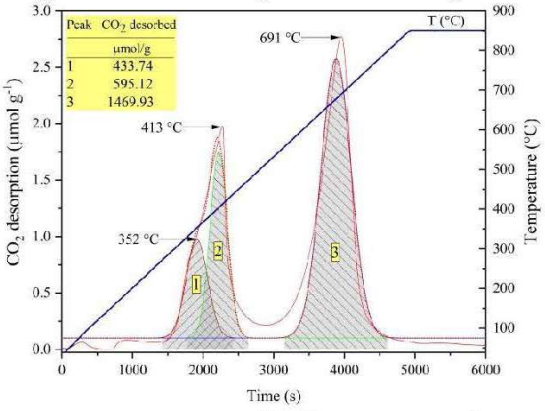

Figure 1. TPD-CO_2 profile of ES-600HD catalyst

ES-600HD catalyst was active in all catalytic tests. Fig. 2 presents the influence of water addition on CaO catalyzed biodiesel production. It is evident that water addition leads to a reduction of induction time and affects the FAME content profile. Compared with similar research [3], such synthesized catalyst remained stable despite water presence, which can cause the formation of non-active hydroxide forms. However, such behaviour could be attributed to the exothermic reaction of CaO and water, which contributed to the simpler breaking of chemical bonds in TAGs molecules forming diacylglycerides (DAG) and monoacidglycerides (MAG), which are the intermediate compounds in the transesterification mechanism.

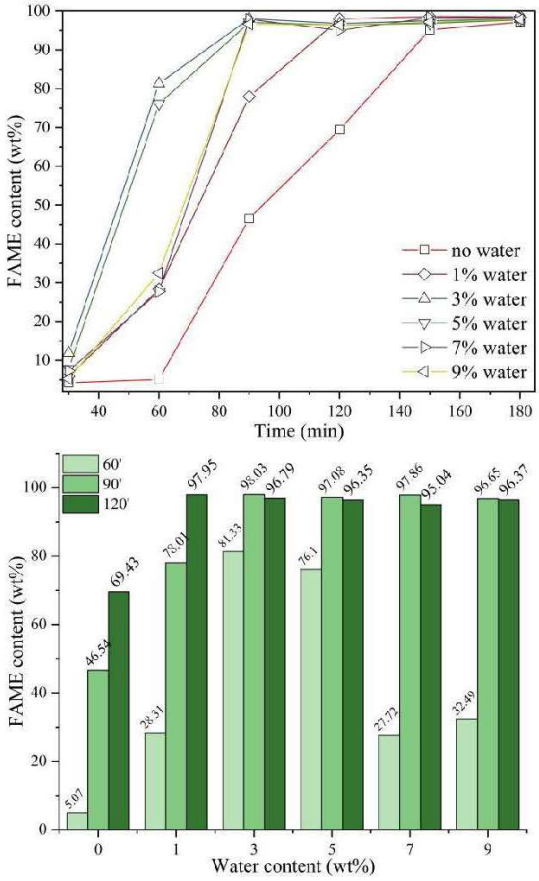

Figure 2. FAME content profiles for different water addition

Addition of water into the reaction affects positively on reaction rate. Considerable reduction in induction time is evident in the case of the water content of 3 wt% and 5wt%. Even with water content higher then 5% reaction rate is higher then in reaction without water, but reaction rate in the induction part is slowing down. However, the reaction equilibrium (FAME content >95%) is achieved in the same time (90 min) in all cases except for synthesis with the water content of 1 wt% and absence of water. It could also be attributed to the different rates of formation of intermediate compounds, which decreases with time, due to the formation of thermodynamically stable crystalline calcium-hydroxide, whereby the reaction takes place on the remaining calcium oxide sites.

Conclusions

From the conducted research, it has been established that

- The synthesized catalyst exhibits a well-defined network of pores and channels adequate for the diffusion of large organic molecules.
- The catalyst exhibits high basicity and well-distributed basic active cites in the medium and high basic regions.
- The catalyst was stable even at high water content (above 5 wt%).
- Water addition leads to a higher reaction rate in the induction period affecting the faster formation of DAGs and MAGs, as intermediate compounds from TAG to FAME.
- The reaction equilibrium (FAME content > 95 %) was achieved for 90 min for all cases except reaction with the water content of 1wt% (120 min) and absence of water (150 min).

References

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