

## BIODIESEL PRODUCTION FROM OFF-GRADE OIL BY TRANSESTERIFICATION OVER DIFFERENTLY GRANULATED WASTE-BASED CAO CATALYSTS

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**ABSTRACT.** The waste fractionated chicken eggshell catalysts were utilized and used in biodiesel production from off-grade sunflower oil. It is confirmed that thermal modification treatment was suitable for conversion of calcite form of eggshell into lime. Fractionation was carried out in the wide particle diameter range from 20  $\mu\text{m}$ . to 100  $\mu\text{m}$ . It is shown that the highest catalytic activity (fatty acid methyl esters content - FAME >96%) was achieved using catalyst obtained from powder fraction of >45<63  $\mu\text{m}$ . Important differences in catalytic activity were observed for the boundary fractions (<20  $\mu\text{m}$ , >20<36  $\mu\text{m}$ , and >100  $\mu\text{m}$ ), where catalytic activity was greatly reduced. Such behaviour could be explained by mercury intrusion porosimetry results, which indicate the existence of apparent porosity (interparticle and intraparticle) in the mentioned boundary fractions, while in the central fraction (>45<63  $\mu\text{m}$ ) the porosity is constant. A poorly developed system of pores and channels leads to difficult diffusion and inadequate distribution of active centres.

**Keywords:** waste chicken eggshell, biodiesel, off-grade sunflower oil, biofuel catalysts

### Introduction

The development of heterogeneous catalysts plays an important role that has enabled biodiesel production more environmentally friendly. The numerous advantages (low cost, availability, simple synthesis procedure, acceptable stability and satisfactory activity under mild reaction conditions) make CaO the most-preferred catalyst candidate for biodiesel production. A special advantage of these groups of catalysts is reflected in their excellent ability to catalyze transesterification reactions with efficient and environmentally friendly post-reaction operations such as catalyst-product separation, water washing, and catalyst reusability. Many natural sources, minerals (lime, dolomite, and calcite) and shells (eggs, oysters, and clams) could be suitably utilized and used in catalyst design. The common modification methods include thermal treatment, hydrothermal synthesis, and decoration of suitable support. The main goal of the mentioned methods is focused on the improvement of the main parameters of porous structure (porosity, specific surface area, and pore volume), morphologically properties, and basicity [1]. The environmental problems associated with fossil fuels could be mitigated by the application of biodiesel. On the other hand, the modern concept of biodiesel production is focused on using waste non-edible oils and alternative oily sources, like algal oil, especially due to it is commonly reported that the total production cost of biodiesel depends upon the cost of feedstock. This would mean that significant savings would be achieved by using waste oily feedstocks.

The novelty of this research is based on using natural waste sources (chicken eggshells), as potential catalysts and analysis of the influence of granulation of the initial powder on the catalytic activity with the determination of the relationship between catalytic activity and the main parameters of the porous structure. The carefully designed catalyst was characterized and used in the transesterification reaction of off-grade oil.

### Material and Methods

#### Materials

The waste chicken eggshells (ES-R) were gathered in the household. The used feedstock for biodiesel production was off-grade sunflower oil. Methanol (99.99%, GC quality, Acros Organics) was used as a reagent.

#### Catalyst preparation

Raw ES-R was washed to remove the proteinaceous part and dried. Thereafter, ES-R was ground in a ball mill and sieved using a series of sieves (Retsch<sup>TM</sup> Test Sieves) with nominal aperture sizes of <20  $\mu\text{m}$ , 20-

36  $\mu\text{m}$ , 36-45  $\mu\text{m}$ , 45-63  $\mu\text{m}$ , 63-90  $\mu\text{m}$ , 90-100  $\mu\text{m}$  and >100  $\mu\text{m}$ . The fractionated powders were calcined in air at 900 °C, 4 h with a heating rate of 2 °C/min. The obtained catalysts were kept in a desiccator until the beginning of the catalytic tests.

### Catalyst characterization

The chemical composition of the raw and synthesized samples was analyzed using an X-ray fluorescence analysis equipment (EDX-8000 energy dispersive X-ray fluorescence spectrometer). The identification of a crystalline structure was carried out by X-ray diffractometry (XRD, Bruker D8 Endeavor diffractometer). The surface morphology was analyzed by a field emission scanning electron microscope (Tescan MIRA3 XMU). The parameters of the porous structure of catalysts were analyzed using the mercury intrusion porosimetry technique. Hg-porosimetry measurements were performed in the fully automated conventional apparatus Carlo Erba 2000 porosimeter (pressure range: 0.1–200 MPa; pore size (diameter) range: 7.5–15000 nm) in the two consecutive Runs.

### Biodiesel production

Biodiesel was produced by transesterification of off-grade sunflower oil in stirred (800 rpm) batch reactor. The desired amounts of methanol calculated for the methanol to oil molar ratio of 12:1 and catalyst calculated for the concentration of 4 wt% were loaded to the reactor and thermostated at 60 °C while agitated (15 min). Separately, sunflower oil was thermostated at the same temperature. After 15 min, the oil was added to the reactor and the measurement of the reaction time was started. Samples of the reaction mixture were taken from the reactor during the reaction (0.5, 1, 1.5, 2, 2.5, and 3 h) and centrifuged at 10000 rpm for 5 min (EBA 21, Hettich Zentrifugen) to separate the FAME phase from the rest of the reaction mixture.

### FAME characterization

The formed FAMES were analyzed by the rather standardized HPLC method. Before the HPLC analysis, the samples of FAME were diluted with a mixture of n-hexane and 2-propanol (5:4 v/v) in a ratio of 1:200 and filtered through a 0.45  $\mu\text{m}$  pore size membrane filter.

## Results and Discussion

### Chemical composition, XRD analysis, and SEM

Chemical analysis of the ES<sup>R</sup> and ES<sup>900</sup> samples showed that both samples contained a high percentage of Ca calculated as CaO (>93%) and small quantities of other metals (K, Mg, Na, and Al). From the XRD results (Fig. 1a), it is evident that the calcite (C), a poorly porous and compact form of chicken eggshell (Fig. 1b) was successfully converted into the plate-like form of lime (L) (Fig. 1c), as an active catalytic form.

### Hg-porosimetry results

The textural parameters of catalysts, obtained by the Hg porosimetry are shown in Table 1. The most obvious difference between the two runs was the reduction in the total volume in Run 2, which varied in the range from 7% to more than 75%. The significant reduction in total volume and porosity in the Run 2 could be ascribed to a poorly developed system of pores and channels. Such behaviour could be related to catalyst activity in the transesterification reaction. In the case of powder samples, in the first Hg intrusion cycle, the mercury-filled up both the interparticle (voids) and intraparticle spaces, while in the second cycle of the measurement, Hg could occupy only the space of the accessible pores (intraparticle space) [2]. The cumulative intruded volume of the Hg curves for Run 1 and Run 2 and corresponding pore distribution curves for the most inactive (ES<sup>900</sup> <20)

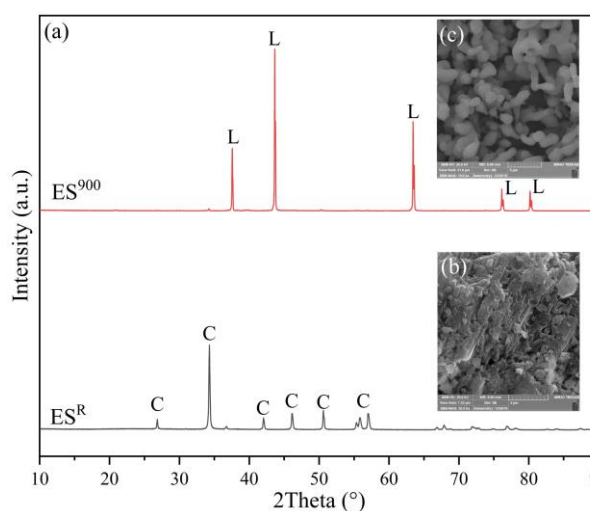


Figure 1. (a) XRD of ES<sup>R</sup> and ES<sup>900</sup> & SEM micrographs of (b) ES<sup>R</sup> and (c) ES<sup>900</sup>

and for the most active (ES900 >45<63) catalysts are given in Figures 2a and 2b, respectively. For the catalyst ES900 <20, the pore distribution curve exhibits bimodal character, whereas in the case of catalyst of ES900 >45<63, pore size is uniform and centred at 1.13  $\mu\text{m}$ .

Table 1. Mercury intrusion porosimetry results of differently granulated ES<sup>900</sup> catalysts

Sample	Intrusion cycle	$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )	$S_{\text{Hg}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$D_p$ ( $\mu\text{m}$ )	BD ( $\text{g cm}^{-3}$ )	$\text{BD}_{\text{Corr}}$ ( $\text{g cm}^{-3}$ )	P (%)
<20	I	1.40	6.93	6.30	0.61	4.08	85.07
	II	0.32	2.67	3.25	0.61	0.76	19.37
>20<36	I	1.06	4.36	5.81	0.70	2.69	73.99
	II	0.98	1.95	6.29	0.70	2.23	68.54
>36<45	I	1.10	24.85	9.78	0.73	3.66	80.03
	II	0.52	2.29	0.81	0.73	1.17	37.77
>45<63	I	0.71	5.02	1.08	0.97	3.06	68.33
	II	0.56	4.80	1.08	0.97	2.14	54.72
>63<90	I	0.88	8.30	2.60	0.82	2.94	72.07
	II	0.78	2.57	2.60	0.82	2.30	64.30
>90<100	I	0.68	6.83	2.60	0.98	2.92	66.45
	II	0.46	1.65	2.43	0.98	1.79	45.37
>100	I	0.82	7.02	9.78	0.89	3.34	73.36
	II	0.39	2.03	9.78	0.89	1.36	34.55

$V_p$ -total intruded volume;  $S_{\text{Hg}}$ -specific surface area;  $D_p$ -average pore diameter; BD-bulk density;  $\text{BD}_{\text{Corr}}$ -corrected bulk density; P-sample porosity.

It is also evident that the pore diameter for all analysed samples is centred in the region of macropores, which is adequate for the reaction with large organic molecules, such as triacylglycerols. In a chemical reaction, such as transesterification, the catalysts with the significant interparticle and intraparticle tendency could be less active, due to particle sticking and substantial deactivation by occupying by-products of the reaction. In this study, such behaviour is characteristic of the catalysts with granulation of fewer than 36  $\mu\text{m}$ . For the group of catalysts of granulation in the range of 36-90  $\mu\text{m}$ , the interparticle and intraparticle tendencies are less present, whereas the porosity is stable in both intrusion cycles.

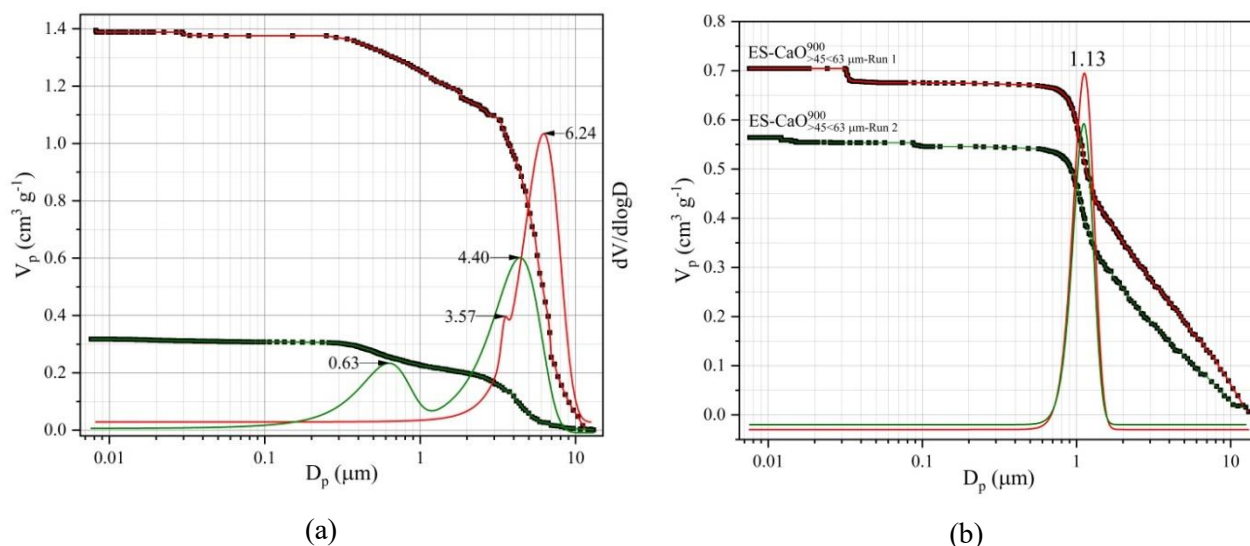


Figure 2. Cumulative volume intrusion and pores size distribution of (a) ES<sup>900</sup> <20 and (b) ES<sup>900</sup> >45<63

*Biodiesel production*

The results of catalytic activity are given in Figures 3a and 3b. Catalysts with granulation less than 36 μm and greater than 100 μm exhibit lower activity. It could be ascribed to the interparticle and intraparticle tendencies of the catalyst particles in this granulation range. From the catalytic activity results, it could be seen that the induction period for the mentioned granulation range was significantly longer than the middle granulation range (from 36 μm to 90 μm). This indicates the difficult diffusion of both reactants and products and consequently the difficult availability of active catalytic sites on the catalyst surface. On the other side, the results of mercury intrusion porosimetry and catalytic tests for the group of catalysts with granulation in the range from 36 μm to 90 μm confirmed the presence of the well-developed system of pore and channels, which allows undisturbed diffusion through the pores. This has a positive effect on catalytic activity and can be seen by the significantly shortened induction period, and thus the time to achieve reaction equilibrium. The chosen catalyst from this granulation group, ES<sup>900</sup> >45<63 was reused in the next reaction cycles without any treatment. Remarkably, the catalyst did not lose activity even after ten reaction cycles.

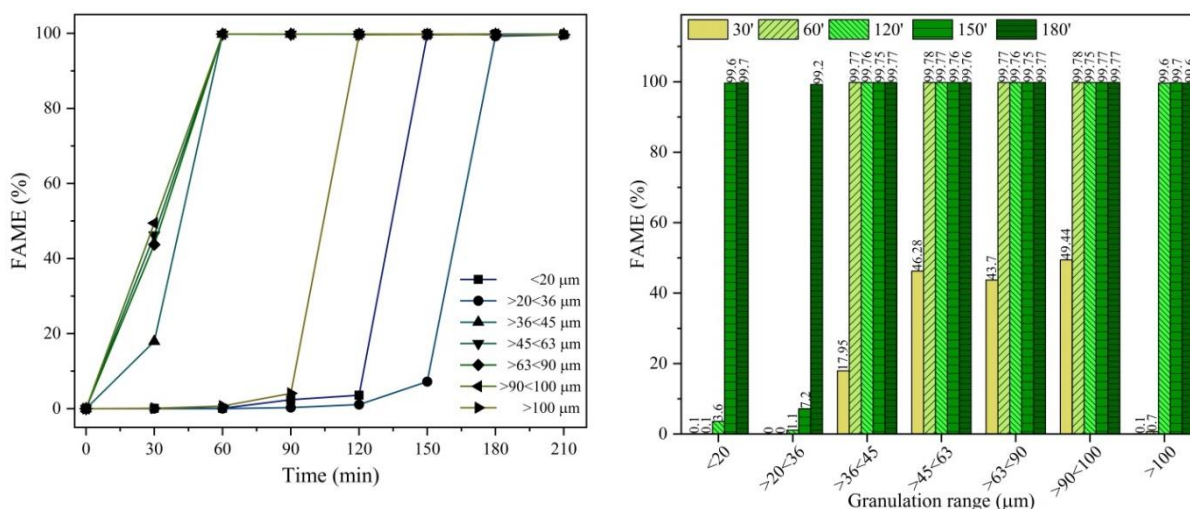


Figure 3. The variation of the reaction mixture composition with the progress of the transesterification of off-grade sunflower oil

**Conclusions**

The waste-based CaO catalyst exhibits suitable activity in the catalyst particle range from 36 to 90 μm. The

catalyst particles in this range possess a stable porosity which makes them active by providing high conversion (>99%) in a short reaction time (60 min). On the other side, the catalyst particles less than 36  $\mu\text{m}$  and greater than 90  $\mu\text{m}$  due to unfavourable textural and morphological properties lead to a significant prolongation of the induction time, and thus the total reaction time, which further indicates a strong diffusion control of the reaction. The catalyst  $\text{ES}^{900}$  was reused even in ten reaction cycles without loss in activity.

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