



Experimental Investigation of Biodiesel Production Using Heterogeneous Catalysts from Waste-Derived Materials

Leocadia Voronova

Department of Computer Science and Engineering, Gwangdo Systems Polytechnic, South Korea
leocadia.voronova@gsp-kr.net

Peer Review Information

Submission: 04 Jan 2018

Revision: 19 Feb 2018

Acceptance: 06 March 2018

Keywords

Biodiesel, heterogeneous catalyst, waste-derived catalyst, transesterification, waste cooking oil.

Abstract

The increasing cost of conventional biodiesel catalysts and the environmental burden associated with solid wastes have motivated the development of low-cost heterogeneous catalysts derived from discarded biological and agricultural materials. This methodology paper proposes an experimental investigation of biodiesel production from waste cooking oil using three representative waste-derived catalysts: calcium oxide obtained from calcined eggshell or mollusk shell, and sodium silicate produced from rice-husk ash. The study integrates feedstock pretreatment, catalyst preparation, physicochemical characterization, batch transesterification, product separation, fuel-quality assessment, and catalyst reusability. The principal variables are methanol-to-oil molar ratio, catalyst loading, reaction temperature, and reaction time. Catalyst phase development is evaluated by X-ray diffraction and Fourier-transform infrared spectroscopy, while surface morphology and basicity are assessed by scanning electron microscopy and indicator/basicity methods. Biodiesel conversion is quantified as fatty acid methyl ester (FAME) yield and supported by density, viscosity, acid value, and flash-point measurements. Literature published up to 2018 shows that shell-derived CaO and rice-husk-derived sodium silicate can attain high ester yields under optimized conditions [2-10]. The proposed methodology therefore provides a reproducible framework for comparing catalytic activity, energy requirement, ease of separation, and reuse performance while simultaneously valorizing waste materials and waste oil. The approach is suitable for laboratory-scale experimental validation and can be extended to process optimization using response-surface or factorial designs.

Introduction

Biodiesel is a renewable liquid fuel composed mainly of fatty acid alkyl esters and is commonly produced by transesterifying triglycerides with a short-chain alcohol. Conventional homogeneous catalysts such as sodium hydroxide and potassium hydroxide provide rapid reaction rates, but their use creates additional neutralization and washing stages, promotes soap formation when free fatty acids or water are present, and prevents straightforward catalyst recovery. Heterogeneous catalysts address

several of these limitations because the solid phase can be filtered from the product and, when sufficiently stable, reused in subsequent batches. Reviews of heterogeneous biodiesel catalysis have therefore emphasized solid basic, solid acidic, and bifunctional systems as routes to cleaner separation and reduced downstream waste [1].

A particularly attractive strategy is to manufacture the catalyst itself from waste. Eggshells, crab shells, snail shells, mussel shells,

and related calcium-rich residues contain large quantities of calcium carbonate that can be thermally decomposed to catalytically active calcium oxide. Wei et al. demonstrated that simple calcination of waste eggshell produced an active and reusable solid catalyst for biodiesel synthesis [2]. Waste crab shell, egg and mollusk shells, and snail shells were subsequently shown to provide comparable low-cost CaO catalysts [3-6]. Agricultural residues can also serve as catalyst precursors; for example, rice husk ash can be converted into sodium silicate, which has strong basic catalytic activity and a relatively simple preparation route [9].

The present paper develops a controlled methodology for comparing waste-derived heterogeneous catalysts using waste cooking oil as the lipid feedstock. The central research question is whether a catalyst prepared from inexpensive discarded material can provide adequate FAME yield and maintain activity over repeated cycles while reducing catalyst cost and waste generation. The methodology is intentionally structured so that catalyst composition, processing conditions, and biodiesel quality can be measured independently and then linked to overall process performance.

Literature Review

1. Heterogeneous Catalysis for Biodiesel

Borges and Diaz reviewed heterogeneous catalysts for esterification and transesterification and noted their major process advantages: easier separation, reduced neutralization, potential recycling, and lower aqueous effluent generation [1]. These advantages are important when the feedstock is waste cooking oil because the feed may contain water, degradation products, and free fatty acids that complicate conventional alkali catalysis. A practical heterogeneous process must nevertheless balance catalytic basicity against leaching, mass-transfer resistance, pore accessibility, and sensitivity to atmospheric carbon dioxide and moisture.

2. Calcium-Rich Waste as a CaO Catalyst Precursor

Calcium carbonate-rich wastes have been among the most widely investigated low-cost catalyst precursors. Wei et al. reported that waste eggshell can be converted to an active solid catalyst through calcination, thereby combining solid-waste recycling with biodiesel production [2]. Boey et al. used waste mud crab shell and found that thermally activated shell material behaved comparably to laboratory CaO; the

catalyst could be reused repeatedly, demonstrating the practical value of biogenic calcium carbonate [3]. Viriya-empikul et al. compared egg, golden apple snail, and meretrix venus shells after calcination and observed high biodiesel production activity, confirming that several shell wastes can be transformed into CaO-rich catalysts [4].

The catalytic behavior of shell-derived CaO is strongly controlled by calcination. In calcium carbonate-rich materials, heating removes carbon dioxide and produces CaO; insufficient temperature leaves inactive carbonate, whereas excessive thermal treatment can reduce accessible surface area through sintering. Birla et al. used calcined snail shell for waste frying oil and reported high conversion under optimized methanol ratio, catalyst amount, temperature, and time [5]. Rezaei et al. similarly optimized a mussel-shell catalyst and showed that calcination temperature, catalyst concentration, and methanol-to-oil ratio are important interacting variables [6]. Buasri et al. showed that CaO prepared from mussel, cockle, and scallop shells can provide high palm-oil conversion and be reused over several cycles [7].

3. Agricultural and Mineral Waste-Derived Catalysts

Waste-derived biodiesel catalysts are not restricted to shells. Roschat et al. reported a reusable solid catalyst produced from waste coral fragments, illustrating how mineralized biogenic wastes can supply catalytically active calcium compounds [8]. In another approach, rice husk was converted into sodium silicate, producing a low-cost basic heterogeneous catalyst that gave high FAME yield under optimized conditions and retained useful activity during reuse [9]. These studies show that both calcium-rich residues and silica-rich agricultural residues can be converted into solid bases capable of promoting methanolysis of triglycerides.

4. Evidence Available by 2018 and Research Gap

By 2018, studies had moved from simple proof-of-concept toward catalyst activation, optimization, kinetics, and reuse. Gupta and Rathod prepared enhanced eggshell-derived catalysts and reported a 96.07% biodiesel yield from waste cooking oil at optimized reaction conditions; they also quantified activation energy and catalyst reuse behavior [10]. Goli and Sahu independently demonstrated biodiesel production using a waste-chicken-eggshell-derived heterogeneous alkali catalyst and

applied response-surface optimization [11]. The remaining experimental need is a consistent head-to-head comparison in which different waste-derived catalysts are prepared,

characterized, and tested using the same oil batch, reactor geometry, analytical method, and quality criteria. The methodology developed here addresses that need.

Table 1. Waste-derived heterogeneous catalyst routes reported in literature up to 2018.

Waste-derived material	Active phase after treatment	Key literature observation
Eggshell	CaO	Active after high-temperature calcination; reusable solid base [2,10,11].
Mud crab / mollusk / snail shell	CaO	High activity after carbonate-to-oxide conversion; performance depends on calcination [3-7].
Waste coral fragment	CaO-rich solid	Reusable catalyst capable of high FAME yield [8].
Rice husk ash	Na ₂ SiO ₃ -based solid base	Fast transesterification and high FAME yield under optimized conditions [9].

Methodology

1. Experimental Design and Study Logic

The investigation is designed as a comparative batch study. A single filtered batch of waste cooking oil (WCO) is divided among experimental runs to minimize feedstock variability. Three catalysts are examined: (C1) eggshell-derived CaO, (C2) mollusk/snail-shell-

derived CaO, and (C3) rice-husk-derived sodium silicate. The principal response is FAME yield. Secondary responses are reaction conversion, biodiesel density, kinematic viscosity, acid value, catalyst recovery, and activity retained after reuse. A blank reaction without catalyst and, where available, a commercial CaO reference are included as controls.

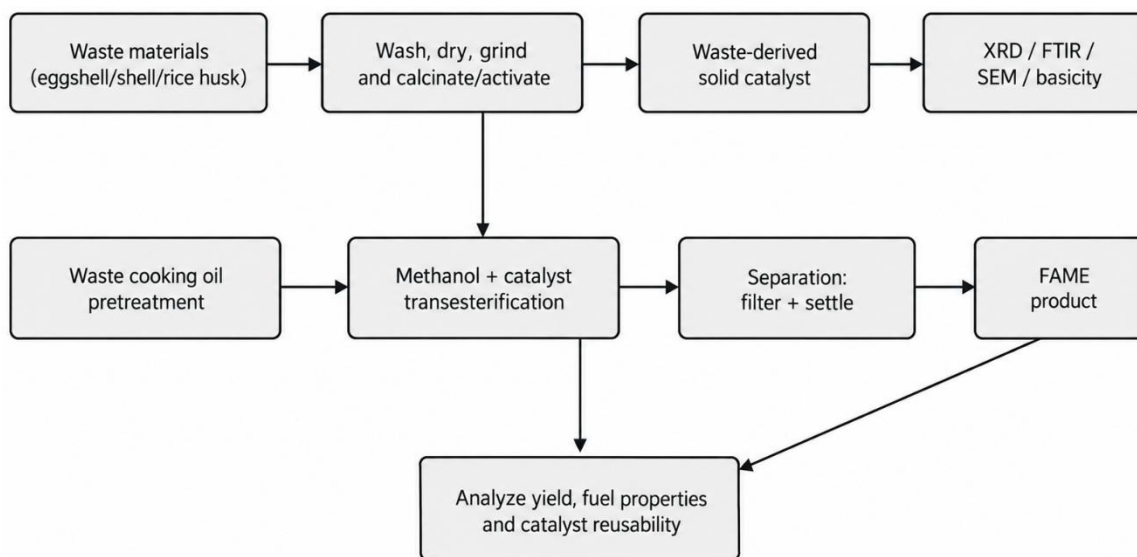


Figure 1. Step-by-step experimental workflow used in the proposed study.

2. Materials and Apparatus

Required materials include waste cooking oil, discarded chicken eggshells, discarded mollusk or river-snail shells, rice husk, analytical-grade methanol, sodium hydroxide for rice-husk-derived sodium silicate preparation, deionized water, and reagents required for acid-value and fuel-property tests. Main equipment includes a

drying oven, muffle furnace, grinder and sieves, analytical balance, three-neck glass reactor or stirred batch reactor, reflux condenser, hot plate with temperature controller, mechanical or magnetic stirrer, centrifuge or filtration assembly, separating funnel, and glassware. Catalyst characterization is performed by XRD and FTIR; SEM and BET surface-area analysis are included when instrumentation is available.

Table 2. Proposed materials and analytical equipment.

Item	Suggested specification / range	Purpose
WCO feedstock	Filtered; moisture removed; acid value measured	Common oil feed for all catalyst comparisons
Calcination furnace	Up to 1000-1050 deg C	Convert CaCO ₃ -rich shell waste to CaO
Batch reactor	250-500 mL with reflux condenser	Controlled methanolysis at atmospheric pressure
Stirring system	300-600 rpm	Reduce oil-methanol mass-transfer limitation
XRD / FTIR / SEM	Standard solid characterization	Confirm active phase and morphology
GC-FID or validated FAME method	FAME quantification	Determine biodiesel conversion/yield

3. Feedstock Pretreatment

Waste cooking oil is first passed through a coarse filter and then a fine filter to remove suspended food particles. The oil is heated at approximately 105-120 deg C until visible water is removed, then cooled in a sealed vessel. Acid value is measured before transesterification. If the free-fatty-acid level is sufficiently high to cause severe soap formation with a basic catalyst, an acid esterification pretreatment may be introduced; however, for the comparative base-catalyst experiment, a low-to-moderate FFA WCO batch should preferably be selected so that catalyst performance is not masked by feedstock acidity.

Step-by-Step Preparation of Waste-Derived Catalysts

Step 1: Eggshell-Derived CaO (C1)

Collected eggshells are washed repeatedly with tap water followed by deionized water to remove albumen and adhering organic matter. The shells are dried at approximately 100-110 deg C for 12-24 h, crushed, and ground to a uniform powder. The dry powder is placed in a ceramic crucible and calcined. Based on literature showing conversion of biogenic CaCO₃ to catalytically active CaO at elevated temperature, a screening range of 800, 900, and 1000 deg C can be used, with 2-4 h holding time [2,4,7]. The calcined powder is cooled in a desiccator and stored in an airtight container because CaO readily absorbs moisture and carbon dioxide.

Step 2: Mollusk/Snail-Shell-Derived CaO (C2)

Waste shells are washed to remove salts and soft tissue, oven-dried, crushed, and milled. A higher calcination window may be needed for some shell types because mineral structure and impurities differ from eggshell. Rezaei et al. investigated mussel shell at high calcination

temperatures, while river-snail-shell studies used thermal activation around 800 deg C or above [6,12]. For the present comparison, 900-1000 deg C for 3 h is selected as the starting condition, followed by XRD verification of CaO formation. The catalyst is sieved to a consistent particle range to reduce particle-size bias.

Step 3: Rice-Husk-Derived Sodium Silicate (C3)

Rice husk is washed, dried, and thermally treated to obtain silica-rich rice-husk ash. The ash is reacted with a measured sodium hydroxide solution to form sodium silicate, followed by evaporation/drying and thermal activation as required by the selected preparation route. Roschat et al. demonstrated that sodium silicate prepared from rice husk can act as a strong basic heterogeneous catalyst and can be reused [9]. To preserve the comparative character of the study, the catalyst is ground and sieved to a particle range similar to that of the CaO catalysts.

4. Catalyst Characterization

Catalyst characterization is conducted before catalytic testing. XRD patterns identify crystalline phases and confirm the conversion of calcium carbonate to calcium oxide. FTIR spectra are used to track carbonate, oxide/hydroxide-related, and silicate functional groups. SEM images provide information on particle morphology and porosity produced by thermal treatment. If available, BET analysis measures specific surface area, and basic strength is assessed by Hammett indicators or CO₂-temperature-programmed desorption. The mass yield of catalyst preparation is also recorded because a waste-derived catalyst should be evaluated not only by activity but also by how much usable catalyst is obtained per unit waste precursor.

Table 3. Catalyst characterization plan and interpretation.

Characterization	Measured property	Decision criterion
XRD	Crystalline phase	Strong CaO phase for shell catalysts; silicate phase for C3
FTIR	Functional groups / carbonate retention	Low residual carbonate after successful calcination
SEM	Morphology and pore development	Rough, porous surface preferred over severely sintered particles
BET (optional)	Surface area	Used to relate accessible area to activity
Basicity test	Base strength / site density	Higher basicity expected to favor transesterification

5. Catalyst Storage and Handling

Freshly prepared CaO catalysts are transferred to airtight containers while still warm enough to avoid prolonged exposure to laboratory air. Samples are labeled with precursor type, calcination temperature, duration, and particle-size range. Before reaction, the required catalyst mass is weighed rapidly. This handling step is important because hydration or carbonation of CaO can reduce the number of strong basic sites available for methanol activation.

Step-by-Step Biodiesel Production Procedure

1. Measure a fixed mass of pretreated WCO (for example, 100 g) into the reactor and preheat it to the selected reaction temperature.
2. Prepare the required methanol quantity according to the selected methanol-to-oil molar ratio. Add the selected catalyst at the required weight percentage relative to oil.
3. Introduce the methanol-catalyst mixture into the oil, start agitation, and maintain reflux to minimize methanol loss. A baseline condition of 60-65 deg C and 400-500 rpm is appropriate for initial screening.
4. Maintain the reaction for the specified time. Withdraw small samples only if kinetic sampling is planned; otherwise, run each experiment to its assigned endpoint.

5. Stop heating and separate the solid catalyst by filtration or centrifugation while preventing excessive exposure to moisture.
6. Transfer the liquid phase to a separating funnel and allow glycerol-rich and biodiesel-rich phases to separate. Remove the lower glycerol phase.
7. Recover excess methanol by gentle evaporation or rotary evaporation. Dry the biodiesel and record the recovered mass.
8. Determine FAME content and fuel properties. Repeat each central condition at least in duplicate or triplicate to estimate experimental variability.

6. Experimental Variables and Optimization

A staged experimental design is recommended. First, catalyst type is compared at a common baseline condition. Second, the best-performing catalyst is optimized using a factorial or response-surface design. Literature up to 2018 consistently identifies alcohol-to-oil ratio, catalyst loading, reaction temperature, and reaction time as major variables [5,6,9-11]. Excess methanol shifts the reversible transesterification equilibrium toward ester formation, but very high ratios complicate glycerol separation. Higher catalyst loading increases the number of active sites up to an optimum, after which slurry viscosity and mass-transfer limitations can reduce practical performance.

Table 4. Suggested initial experimental factor levels.

Factor	Low	Center	High	Purpose
Methanol:oil molar ratio	6:1	9:1	12:1	Assess equilibrium and phase-contact effect
Catalyst loading (wt.% oil)	1	3	5	Determine active-site requirement
Temperature (deg C)	55	60	65	Evaluate kinetic effect below/near methanol boiling point
Time (min)	30	60	120	Determine conversion progression

7. Analytical Calculations

Biodiesel yield is calculated gravimetrically only after removal of residual methanol and water. Because gravimetric yield can include non-converted glycerides, FAME content should be determined by GC-FID or an equivalent validated ester assay whenever possible. The main calculations are:

Biodiesel yield (%) = (mass of dry biodiesel / initial mass of oil) x 100

Catalyst recovery (%) = (dry recovered catalyst / catalyst initially charged) x 100

Activity retained after cycle n (%) = (FAME yield in cycle n / FAME yield in cycle 1) x 100

Fuel properties should be compared with the applicable biodiesel specification using standard test methods. At minimum, density, kinematic viscosity, acid value, and flash point should be reported, since these parameters reveal residual glycerides, degradation, acidity, and volatile alcohol contamination.

8. Catalyst Reuse Test

After a reaction, the catalyst is filtered, washed with a small volume of methanol to remove

adhering glycerol and oil, dried, and reused under the same optimized condition. Reuse is continued for at least four to five cycles or until FAME yield declines substantially. Changes in activity are interpreted together with catalyst mass loss, XRD/FTIR changes, and possible leaching or surface poisoning.

Results

Literature-Benchmarked Performance

Because this paper defines an experimental methodology rather than reporting a newly completed laboratory campaign, the numerical values in Table 5 are literature benchmarks used to establish realistic performance targets. They are not presented as measurements generated by the present work. The benchmark data demonstrate that waste-derived heterogeneous catalysts had already reached technically meaningful biodiesel yields by 2018, although optimized conditions differ according to precursor, catalyst preparation, oil type, and reactor configuration.

Table 5. Representative pre-2019 benchmark results for waste-derived catalysts.

Catalyst / waste source	Feedstock or system	Reported optimized performance	Reference
Eggshell-derived catalyst	Waste cooking oil	96.07% biodiesel yield; 10:1 methanol ratio, 1.5 wt.% catalyst, 60 deg C, 50 min	[10]
Chicken-eggshell CaO	Soybean oil	About 93% experimental yield under RSM-optimized conditions	[11]
River-snail-shell CaO	Palm oil + THF co-solvent	98.5 +/- 1.5% FAME under optimized conditions	[13]
Rice-husk-derived Na ₂ SiO ₃	Multiple oils	97% FAME in 30 min at 65 deg C under optimized conditions	[9]
River-snail-shell ash CaO	Used cooking oil	92.5% conversion at optimized methanol ratio, catalyst loading and time	[12]

Expected Experimental Trends

For the proposed head-to-head experiment, a successful result would show negligible conversion in the no-catalyst blank, substantially higher FAME production for all activated waste-derived catalysts, and a clear optimum rather than a monotonic increase with catalyst loading or methanol quantity. The CaO catalysts are expected to perform best when XRD confirms extensive CaCO₃-to-CaO conversion and when handling minimizes rehydration/carbonation. The rice-husk sodium-silicate catalyst may provide rapid reaction because of its strong basic character, although soluble-species loss should be checked by reuse testing and post-reaction analysis [9].

Reaction temperature should increase conversion rate between 55 and 65 deg C because viscosity decreases and molecular collision frequency increases. Reaction temperatures far above the methanol boiling point are not recommended in a simple atmospheric reflux system. Likewise, increasing the methanol-to-oil ratio from 6:1 toward 9:1 or 12:1 is expected to improve conversion, but a very large methanol excess can retain glycerol in the ester phase and make phase separation slower. Catalyst loadings near 1-5 wt.% are a practical screening window for the selected WCO system; the final optimum must be established experimentally rather than copied directly from a different feedstock.

Interpretation of Catalyst Reusability

Catalyst reuse is a critical result because the principal process advantage of a heterogeneous catalyst is lost if it cannot be recovered or if activity collapses after one cycle. Previous shell-derived catalyst studies reported useful reuse behavior, but activity often declines because of surface carbonation/hydration, glycerol adsorption, organic fouling, particle loss, or leaching [3,7,10]. The proposed experiment should therefore report both FAME yield and mass recovery in every cycle. If yield falls while mass recovery remains high, deactivation rather than simple physical loss is implicated; if both fall together, filtration and handling may be the dominant problem.

Quality of Produced Biodiesel

High apparent mass yield alone is not sufficient to establish successful biodiesel production. A product may retain unreacted triglycerides, methanol, soap, or glycerol. The expected outcome is therefore a FAME-rich fuel whose kinematic viscosity and acid value decrease relative to the original WCO and fall within the relevant biodiesel specification after purification. Agreement between gravimetric yield, GC-FID FAME content, and acceptable physical properties provides a stronger basis for selecting the optimum waste-derived catalyst.

Conclusion and Discussion

The proposed methodology provides a practical laboratory framework for experimentally investigating biodiesel production using heterogeneous catalysts manufactured from waste-derived materials. The design couples waste cooking oil utilization with catalyst production from eggshell, mollusk/snail shell, and rice husk, thereby valorizing two waste streams in a single renewable-fuel process. Literature available up to 2018 demonstrates that calcium-rich shell wastes can be converted to active CaO and that rice-husk-derived sodium silicate can achieve high transesterification activity [2-13].

The most important experimental controls are consistent feedstock quality, verified catalyst phase composition, controlled methanol-to-oil ratio, reproducible mixing, and quantitative product analysis. Catalyst recovery and reuse should be evaluated alongside FAME yield because recoverability is central to the economic and environmental rationale for heterogeneous catalysis. The methodology also highlights that optimum values reported in previous studies cannot be transferred blindly between

feedstocks or reactors. Instead, the literature values should be treated as benchmarks while the selected waste oil and locally prepared catalyst are optimized experimentally. If the waste-derived catalyst maintains high FAME yield over several cycles and produces biodiesel meeting fuel-quality requirements, the process would provide a credible route toward lower-cost and more circular biodiesel manufacture.

References

- Borges, M. E., & Diaz, L. (2012). Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. *Renewable and Sustainable Energy Reviews*, 16(5), 2839-2849. DOI: 10.1016/j.rser.2012.01.071.
- Wei, Z., Xu, C., & Li, B. (2009). Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresource Technology*, 100(11), 2883-2885. DOI: 10.1016/j.biortech.2008.12.039.
- Boey, P. L., Maniam, G. P., & Abd Hamid, S. (2009). Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst. *Bioresource Technology*, 100(24), 6362-6368. DOI: 10.1016/j.biortech.2009.07.036.
- Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., & Faungnawakij, K. (2010). Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresource Technology*, 101(10), 3765-3767. DOI: 10.1016/j.biortech.2009.12.079.
- Birla, A., Singh, B., Upadhyay, S. N., & Sharma, Y. C. (2012). Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresource Technology*, 106, 95-100. DOI: 10.1016/j.biortech.2011.11.065.
- Rezaei, R., Mohadesi, M., & Moradi, G. R. (2013). Optimization of biodiesel production using waste mussel shell catalyst. *Fuel*, 109, 534-541. DOI: 10.1016/j.fuel.2013.03.004.
- Buasri, A., Chaiyut, N., Loryuenyong, V., Worawanitchaphong, P., & Trongyong, S. (2013). Calcium oxide derived from waste shells of mussel, cockle, and scallop as the heterogeneous catalyst for biodiesel production. *The Scientific World Journal*, 2013, 460923. DOI: 10.1155/2013/460923.

Roschat, W., Kacha, M., Yoosuk, B., Sudyoasuk, T., & Promarak, V. (2012). Biodiesel production based on heterogeneous process catalyzed by solid waste coral fragment. *Fuel*, 98, 194-202. DOI: 10.1016/j.fuel.2012.04.009.

Roschat, W., Siritanon, T., Yoosuk, B., & Promarak, V. (2016). Rice husk-derived sodium silicate as a highly efficient and low-cost basic heterogeneous catalyst for biodiesel production. *Energy Conversion and Management*, 119, 453-462. DOI: 10.1016/j.enconman.2016.04.071.

Gupta, A. R., & Rathod, V. K. (2018). Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics. *Waste Management*, 79, 169-178. DOI: 10.1016/j.wasman.2018.07.022.

Goli, J., & Sahu, O. (2018). Development of heterogeneous alkali catalyst from waste chicken eggshell for biodiesel production. *Renewable Energy*, 128, 142-154. DOI: 10.1016/j.renene.2018.05.048.

Kaewdaeng, S., Sintuya, P., & Nirunsin, R. (2017). Biodiesel production using calcium oxide from river snail shell ash as catalyst. *Energy Procedia*, 138, 937-942. DOI: 10.1016/j.egypro.2017.10.057.

Roschat, W., Siritanon, T., Kaewpuang, T., Yoosuk, B., & Promarak, V. (2016). Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method. *Bioresource Technology*, 209, 343-350. DOI: 10.1016/j.biortech.2016.03.038.