

## Active Heterogeneous CaO Catalyst Synthesis from *Anadara granosa* (Kerang) Seashells for *Jatropha* Biodiesel Production

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**Abstract.** Heterogeneous catalysts are often used at large to produce biodiesel from non-edible vegetable crude oils such as *Jatropha curcas* oil (JCO). In this study, an active heterogeneous CaO catalyst was synthesized from a tropical biodiversity seashells *Anadara granosa* (*A.granosa*). The catalytic efficiency of *A.granosa* CaO was investigated in transesterification of JCO as biodiesel. The *A.granosa* CaO catalyst was synthesized using 'Calcination – hydration – dehydration' protocol. The spectral characterization of the catalyst were investigated by employing FT-IR, SEM, BET and BJH spectrographic techniques. The experimental design was executed with four reaction parameters that include catalyst concentration (CC), methanol ratio (MR), transesterification time (TT) and reaction temperature (RT). The JCO transesterification reactions as well as impact of reaction parameters on the *Jatropha* biodiesel yield (JBY) were analyzed. The sufficiency of the experimental results conformed through sequential validation tests, as a result, an average of 96.2% JMY was noted at optimal parametric conditions, CC of 3wt. %, TT of 120 min, MR of 5 mol. and RT of 60°C at a constant agitation speed of 300rpm. An average JMY of 87.6% was resulted from the *A.granosa* CaO catalyst during their recycling and reuse studies up to third reuse cycle.

### 1 Introduction

Ever increasing energy needs for the world's comprehensive developments emphasis on intrinsic and sustainable approaches into multiphase coherent and seamless research for the future[1]. On the contrary, despite substantial policy and research initiatives, the global warming, pollution as caused by the fossil fuel combustion emissions besides depletion of natural petroleum deposits reiterates search for renewable and alternate fuel and energy sources. In early 1980's the biodiesels were commercially launched as an alternate fuel in the view of minimizing the greenhouse exhaust gas emissions[2]. The renewable feed stocks such as edible and non-edible vegetable oils, algae oils, animal fat wastes etc.[3,4] were prominent in biodiesel production by their transesterification with methanol and a catalyst. To minimize the demand for edible oils and to maintain sustainable human food cycle, non-edible feed stocks such as *Jatropha curcas*, a euphorbia family plant mainly grown in tropical and sub-tropical regions, has accomplished both commercial and researcher's attention, besides the plants supplementary benefits[4].

A large number of homogeneous and heterogeneous catalysts were experimentally utilized in transesterification of various vegetable oils and among which heterogeneous catalysts demonstrated higher catalysis, stability, reusability and ease in production mechanisms[5,6]. An adequate usage of catalysts as

synthesized from diverse sources of wastes is crucial as part of the sustainable and strategic management of wastes and so as the environmental concerns[7,8]. Many researchers have reported on calcium based catalysts synthesized by make use of direct calcination over a temperature range of 800°C – 900°C from domestic waste shells such as cockle shells[9], *Pomacea* sp. shells[10] derived CaO from mussel shells[11], waste chicken-eggshell[12], ostrich-eggshell[12] etc. and utilized effectively in transesterification. These reports emphasizes CaO catalysts prominence in catalysis of triglycerides of oils to biodiesel. Since the domestic chicken eggshells are notably abundant, economic synthesis of catalysts from these waste shells encompasses the recycling of wastes for sustainability and environmental advantages as well. *Anadara granosa* (*A.granosa*) seashells are prominent and economic edible protein source in the Indo-Pacific tropical region especially from wetlands of Kuching[13] and Asajaya[14] areas in Sarawak state and also in other coastal areas of Malaysia. *A.granosa* shells are largely available in the region and locally known as 'Kerang'[13,14]. According to our literature review, any research was published on synthesis of heterogeneous CaO catalyst.

The present research reports on CaO synthesis with higher surface area form *A.granosa* seashells to produce an active CaO heterogeneous catalyst. 'Calcination – hydration – dehydration' protocol was employed for

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economic catalyst synthesis and the catalyst was fully characterized by spectrographic techniques. The synthesized CaO Catalytic activity was tested in transesterification of the *Jatropha curcas* oil (JCO). The *Jatropha* biodiesel yield (JBY) optimization was achieved through analysis of four principal reaction parameters include catalyst concentration, methanol ratio, transesterification time and reaction temperature. The *A.granosa* CaO catalyst reusability together with economic catalyst synthesis in comparison with a commercial CaO were investigated.

## 2 Experimental

### 2.1 Materials

The *Jatropha curcas* oil (JCO) used for biodiesel production was extracted from their seeds using oil expelling machine without purification and or refining. The JCO saponification (SV) and acid values (AV) were calculated by adopted a standard procedure[15] and noted as 210.04 mg KOH/g and 29.46 mg KOH/g respectively. The JCO molecular weight (M) =  $(56.1 \times 1000 \times 3)/(SV - AV)$ [15] resulted as 932 g/mol. All experiments were performed using laboratory grade chemicals that include potassium hydroxide 95%, methyl alcohol >99%, calcium oxide CAS.NO.0001305788 and sulfuric acid 99.9%. The experimental protocol was designed and executed at the energy lab, mechanical and manufacturing engineering department, faculty of engineering, Universiti Malaysia Sarawak (UNIMAS), Malaysia.

### 2.2 Catalyst synthesis

The *A.granosa* shells were collected from a local market then carefully rinsed simultaneously with tap, hot and distil water to clean up the edible organic fractions adhered to the eggshells as well as other impurities. The *A.granosa* shells were overnight dried at 105°C[16] in a hot-air oven then grounded using a domestic blender and sieved through 80µm mesh. The shells powders were calcined at 900°C for 2hrs utilizing a muffle furnace (KSL-1700X-A4, MTI Corporation, USA). The *A.granosa* shells derived CaO were refluxed in distilled water continuously for 6hrs at 60°C. The filtered calcium solid particles were overnight dried in a hot-air oven at 120°C further finely grounded for 3hrs by employing a ball mill with an operating speed of 200rpm. The fine calcium particles were recalined for 3hrs at 600°C to dehydrate the hydroxides and to form calcium oxides. The powders were dehydrated for 1hr in a hot air oven at 100°C to make it free from working atmosphere effects, before being used as a catalyst. Thus, an active heterogeneous CaO catalyst from *A.granosa* shells was synthesized subjected to the 'Calcination–hydration–dehydration' synthesis protocol.

### 2.3 CaO catalyst characterization

To analyse the chemical features of synthesized CaO sample particles FT-IR: Fourier Transform Infrared, Spectrophotometer (Perkin Elmer Model 100 series) was employed and tested over a wavelength region of 4000 to 280 cm<sup>-1</sup>. The particle morphology was studied using a SEM: scanning electron microscopy (Hitachi TM3030). Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda(BJH) (Quantachrome iQ-AG-C) were utilized to examine the catalyst surface area pore diameter and pore volumes respectively.

### 2.4 Catalyst economic synthesis study

The economic synthesis of CaO from *A.granosa* shells was carried out considering the raw *A.granosa* shells as procured from the market together with CaO synthesis costs at laboratory scale. The price of *A.granosa* shells synthesized CaO was compared with price of a commercial CaO (CAS number: 0001305788).

### 2.5 Experimental design for biodiesel production

*Jatropha* biodiesel was produced from JCO following a two-step transesterification based on many preliminary laboratory experiments to analyze all-important parameters such as catalyst concentration (CC), transesterification time (TT), methanol ratio (MR), and reaction temperature (RT) were ascertained and analyzed in contrast with previous studies reported in the literature[15,16]. An in-house laboratory protocol was followed for biodiesel synthesis, in brief free fatty acid (FFA) analysis, acid esterification and transesterification together with methanol and catalyst mixture, separation of glycerol, washing and drying. FFA of a vegetable oils impacts on their transesterification reactions during biodiesel production[17,18]. 29.3% of FFA was measured from the JCO samples by following a standard method as described our recent work published[19]. Since the oil samples have reported a very high FFA, which lead to lowering the biodiesel yield, especially, in solid heterogeneous catalyzed transesterification[18–20]. Acid esterification of JCO was carried out in the presence of H<sub>2</sub>SO<sub>4</sub> and methyl alcohol to reduce the JCO FFA to 1% which is suitable for base catalyzed transesterification[21].

Transesterification reaction firstly transforms the triglycerides of JCO samples to diglycerides and then to monoglyceride and methyl esters (biodiesel) subsequently as a final product in three consecutive reactions which are equivalent and reversible in nature. *A.granosa* shells synthesized CaO catalyzed biodiesel reaction was carried out with esterified JCO. The catalyst and methanol mixture were prepared in accordance with oil ratio by volume. The transesterification reaction process operating ranges were comprehend with state of the art literature[18,19,22]. The reactant mixture contents were allowed to react over a course of transesterification

four variables catalyst concentration (CC: 1% - 6 %wt.), transesterification time (TT: 30min. – 180 min), methanol ratio (MR: 1 – 6 mol.), and reaction temperature (RT: 35°C-65°C) at constant agitation speed of 300rpm with a magnetic stirrer. The catalyst was collected from the mixture with a centrifuge while glycerol and biodiesel layers were separated followed by warm deionized double distilled water wash and heating in order to obtain pure biodiesel.

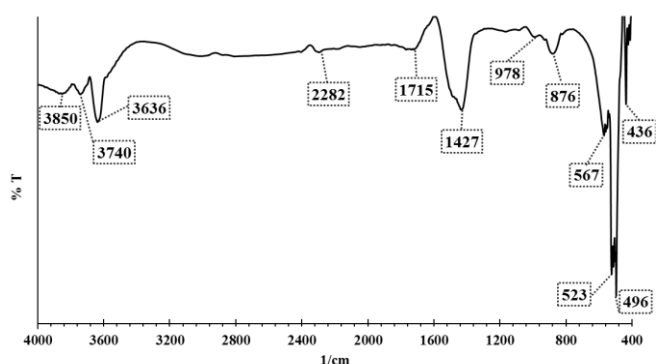
## 2.6 Catalyst reusability study

Transesterified JCO and other mixtures were centrifuged at 3500rpm for 1hr to recover *A.granosa* shells CaO. The solid precipitate was thoroughly washed using n-hexane successively for four times to prepare an impurities free catalyst and oven dried for 24hrs. The recovered CaO was recalcined for 2hrs at 600°C before using in transesterification of JCO.

## 3 Results and discussion

### 3.1 Catalyst characterization analysis

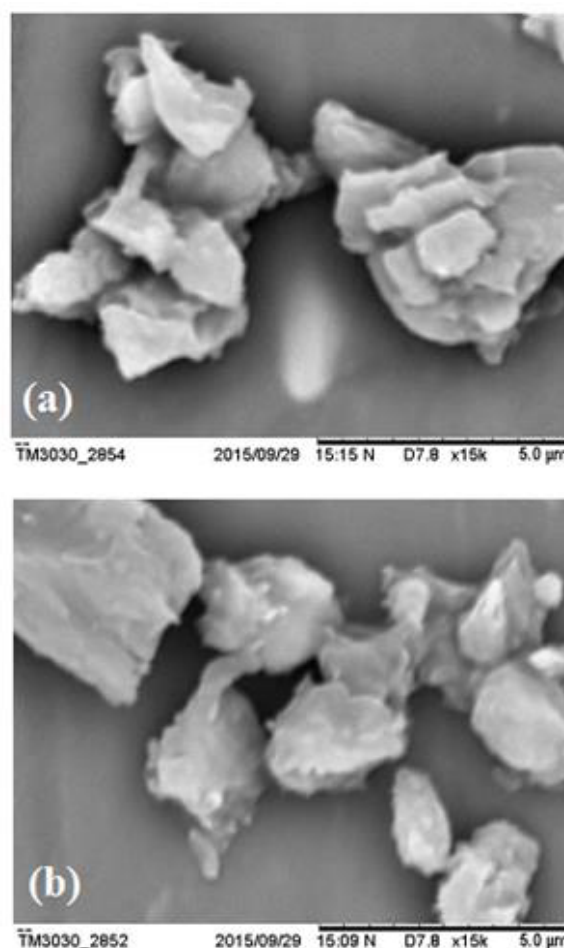
The infrared (IR) spectrum of CaO catalyst as synthesized from *A.granosa* shells was graphically shown in Figure 1. It's evident that Ca-O group absorptions were strongly attributed over wavenumbers  $<600\text{cm}^{-1}$ , along with medium bands at  $1427\text{cm}^{-1}$  and  $876\text{cm}^{-1}$ , as well as weak bands at  $3740\text{cm}^{-1}$ ,  $3850\text{cm}^{-1}$  and  $978\text{cm}^{-1}$ . A Sharp absorption peak at  $1427\text{cm}^{-1}$  corresponds a carbonyl group due to their asymmetrical stretching vibration[23]. The carbonyl and hydroxyl group traces were exist in the IR spectrograph due to absorption of carbon dioxide and moisture on to the calcined CaO samples from the atmosphere[10].



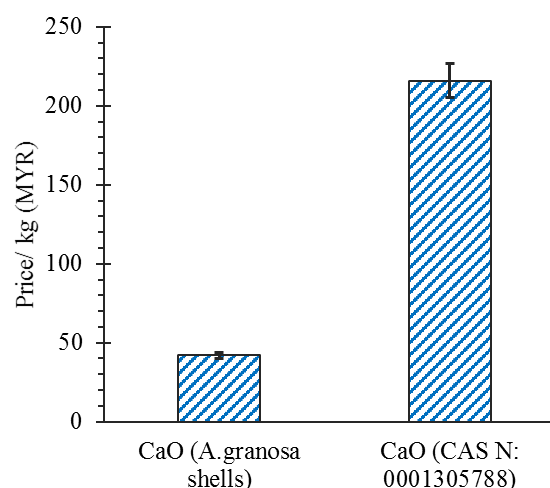
**Figure 1.** IR Spectrum of *A.granosa* shells synthesized CaO catalyst

The SEM monograms in Figure 2 (a-b) shows morphology and active sites of calcined CaO particles synthesized from *A.granosa* shells. The CaO particle monograms illustrates presence of uneven particle surfaces and hence formation of a porous catalyst structures. As a result, the calcined CaO agglomerations could provide highly active surfaces. The surface area of CaO particles synthesized from *A.granosa* shells together

with their average pore diameter and pore volume were noted from the BET and BJH results  $34.6\text{ m}^2/\text{g}$ ,  $9.151\text{ nm}$  and  $0.012\text{ cc/g}$  respectively. The catalyst pore diameter represents mesopores it would show cases higher suitability for catalytic reactions[24]. Further, these results significantly agrees higher specific surface area of CaO particles by which catalyst catalytic activity improves in transesterification of triglycerides to methyl esters and hence the synthesized catalyst is stated as an active catalyst[24].



**Figure 2.** SEM spectral monograms of *A.granosa* shells CaO particles



**Figure 3.** *A.granosa* shells CaO synthesis cost analysis in comparison with commercial CaO.

**Table 1.** Jatropha biodiesel yield % w.r.t. variation in transesterification reaction parameters

Catalyst concentration (CC)		Methanol ratio (MR)		Transesterification time (TT)		Reaction temperature (RT)	
CC (wt. %)	JBY %	MR (mol.)	JBY %	TT (min.)	JBY %	RT (°C)	JBY %
1	78	1	57	30	81	40	75
2	93	2	60	60	90	45	83
3	97	3	70	90	93	50	89
4	88	4	84	120	96	55	92
5	74	5	96	150	88	60	97
6	68	6	94	180	82	65	93

### 3.2 *A.granosa* Catalyst synthesis economic analysis

The CaO synthesis cost from *A.granosa* shells was calculated based on the raw shells as well as approximate laboratory synthesis costs and compared with market price of a commercial CaO (CAS number: 0001305788) as shown in Figure 3. The *A.granosa* shells synthesized CaO was found to be more economic than the commercial CaO. The major cost difference may be due to usage of very low cost raw materials as well as customized synthesis protocols adopted at the laboratory.

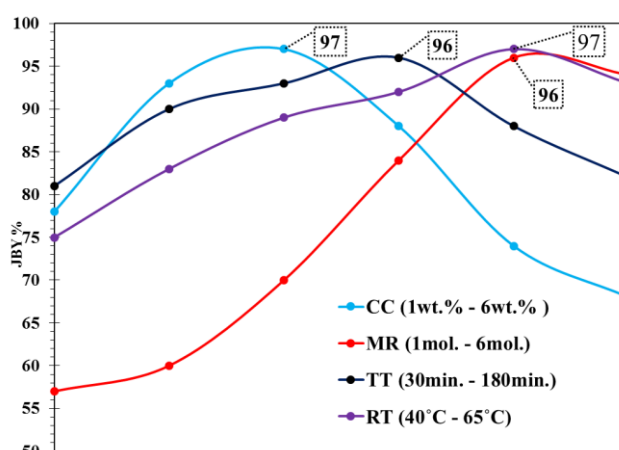
### 3.3 Jatropha biodiesel production analysis

The biodiesel production metrics using *A.granosa* shells CaO from JCO were tabulated Table 1. The experimental results of Jatropha biodiesel yield (JBY) percentage with respect to each of transesterification reaction parameter performed were plotted in Figure 4. The catalyst concentration influences the biodiesel yield at large together with other factors. The JMY% was incremental within 1wt. % - 3wt. % of CC and resulted a maximum JBY of 97% at 3wt. %. However, further increase in CC resulted in lowering the JBY as a result of soap formation and secondary reactions[25].

Methanol ratio is a primary parameter in transesterification of vegetable oils. The results from both Table 1 and Figure 4 demonstrates the relevance of higher MR i.e. 5 mol. yields 96% of biodiesel. A reduction in JMY% was noted beyond 5 mol. of MR, which may be a result of reversible reaction due to the presence of excess over methanol[26]. The transesterification time for biodiesel production was a collective impact of other reaction parameters[27,28]. JMY% as obtained from the experiments shows, Figure 4, 120 min. of TT yields 96% biodiesel which is maximum. Experiments run 120 min. reveals a decrease in JMY as the excessive TT destabilizes the state of reaction equilibrium besides emergence of soap formation[27,29,30] and hence on the JMY as well.

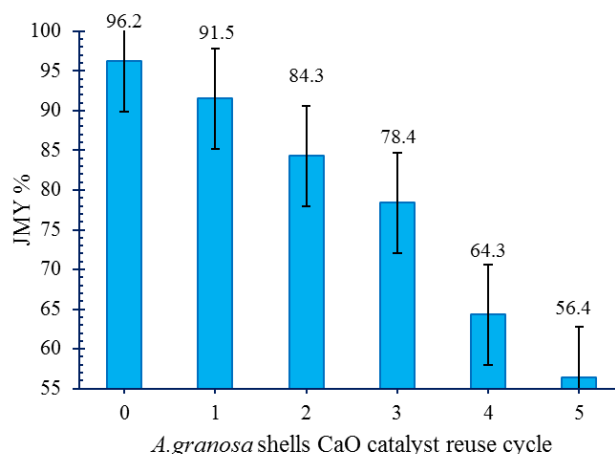
The biodiesel production was testified over 35°C-65°C reaction temperature (RT). At 60°C of RT a maximum JMY of 97% was reported. Reaction kinetics are

considered to be accelerated at elevated RT, however viscosity JCO predominantly minimizes which further leads to soap formation as well as lowering the JMY[3]. Furthermore, temperatures over 60°C were close to the methanol's boiling point 64.7°C, consequently expedites methanol evaporation which further curtails their availability for completing the reaction[27,31].



**Figure 4.** Graph showing Jatropha biodiesel yield % vs transesterification parameters

From the experimental result analysis, the optimal parameters contributed for maximum JMY% were noted. A series of four confirmatory experiments were performed simultaneously at CC of 3wt. %, TT of 120 min, MR of 5 mol. and RT of 60°C at a constant agitation speed of 300rpm, as a result, an average of 96.2% JMY was noted.



**Figure 5.** *A.granosa* shells synthesized CaO catalyst reusability study over five reuse cycles.

### 3.4 *A.granosa* Catalyst reusability analysis

The *A.granosa* shells synthesized CaO catalyst reusability in transesterification of JCO was studied over optimal reaction conditions that include CC of 3wt. %, TT of 120 min, MR of 5 mol. and RT of 60°C at a constant agitation speed of 300rpm. During five catalyst reuse cycles conducted successively, the JMY was reducing from each of their previous reuse cycle as depicted in Figure 5. This may be due to the fact that losing of active sites present in the *A.granosa* shells synthesized CaO as well as agglomerations formed out of catalyst particles and JCO. However, the *A.granosa* shells synthesized CaO catalyst was stable and yields 78.4% of biodiesel after third reuse cycle.

## 4 Conclusions

In this research, an active heterogeneous CaO catalyst was successfully synthesized from a tropical biodiversity seashells *Anadara granosa* (*A.granosa*). The *A.granosa* CaO catalyst was synthesized by following ‘Calcination – hydration – dehydration’ protocol. The spectral characterizations of the synthesized catalyst were investigated using FT-IR, SEM, BET and BJH spectrographic techniques. The SEM and BET results reveals presence of mesopores uneven particle surfaces with an average pore diameter and pore volume of 34.6 m<sup>2</sup>/g, 9.151 nm and 0.012 cc/g respectively. The *A.granosa* CaO catalytic efficiency was studied over transesterification of JCO as biodiesel considering catalyst concentration (CC), methanol ratio (MR), transesterification time (TT) and reaction temperature (RT). An average of 96.2% JMY was noted as optimal, at CC of 3wt. %, TT of 120 min, MR of 5 mol. and RT of 60°C at a constant agitation speed of 300rpm. In the *A.granosa* CaO catalyst recycling and reuse an average JMY of 87.6% was resulted up to third reuse cycle.

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