

# Comparative Evaluation of the Ultrasound-Assisted and Microwave-Assisted Transesterification of WVO Using Sodium Impregnated Oyster Shell as Catalyst

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**Abstract**— Biodiesel was produced from waste vegetable oil under ultrasound-assisted transesterification and microwave-assisted transesterification using sodium impregnated oyster shell catalyst. The catalyst was prepared by impregnation method using different concentrations of Sodium Hydroxide Solution. Hammett indicators, Infrared Spectroscopy (IR) and X-ray Diffraction (XRD), were used to evaluate the characteristics of the catalysts. The catalysts were easily separated from WVO biodiesel mixture by filtration and reuse is possible without drop in its efficiency. The maximum Fatty Acid Methyl Ester (FAME) yield of biodiesel during ultrasound-assisted transesterification was 82% while maximum FAME yield in microwave assisted transesterification was 80%. Optimum process parameters were identical to both processes except reaction time. The optimum methanol to oil ratio = 15:1 and catalyst load = 20%. Optimum reaction time for ultrasound-assisted transesterification was 20 minutes at ultrasonic percent amplitude of 40%. Optimum reaction time for microwave-assisted transesterification was 15 minutes at microwave output power of 600 watts.

**Keywords**— Biodiesel; catalyst; transesterification; ultrasound; methyl ester.

## I. INTRODUCTION

Biofuel had been studied as one possible solution in the imminent depletion of fossil fuels. It is widely regarded to be eco-friendly and very sustainable (Demirbas 2009). Biodiesel, a form of biofuel, is produced by transesterification of oils or fats derived from plant matter or animal wastes. Use of biodiesel also has potential environmental impact. While fossil fuels just emit CO<sub>2</sub>, biodiesel derived from plants makes use of CO<sub>2</sub> in the atmosphere in its photosynthesis (Ma and Hanna 1999). Moreover, biodiesel does not emit sulfur or aromatic based compounds and it has a lower hydrocarbon, carbon monoxide and particulate matter emission. In total, biodiesel has 41% lesser GHG emission when compared to diesel (Meher, Vidya Sagar, and Naik 2006).

The current feedstock available for biodiesel production is rapeseed, palm, corn, peanut, canola, and soybean oils. The issue with biofuel production is that it competes with food production (Issariyakul and Dalai 2014). Implications such as raising food prices due to higher demand and increased deforestation to clear more land for plant cultivation is highlighted. Since the cost of the raw materials attribute to about 60-80% of the total cost of biodiesel production, the choice of cheaper feedstock with high lipid content had driven researchers to a more viable feedstock, microalgae (Raslavičius et al. 2014). The use of lipid source coming from wastes and cheap materials had become a better

alternative in the production of biodiesel production. Waste vegetable oil is one of those sources that are common everywhere and are cheaper. More importantly, waste vegetable oil is already considered waste where the disposal of such are considered to be an environmental issue. One way of combating these issue is making these so called waste into something more productive, and in these case converting them into fuel.

The common transesterification reaction just requires mixing the oil, alcohol, and catalyst at a temperature just below the boiling point of alcohol. A few technologies had been incorporated into this set-up to increase the yield of the product and to decrease the reaction time (Pragya, Pandey, and Sahoo 2013). One of these technologies is the use of microwave. Microwave transfer energy into the algae-solvent mixture by dipolar polarization, ionic conduction, and interfacial polarization mechanisms. It will produce heat and pressure within the mixture and force out the lipids from the biological matrix in a lesser amount of time (Patil, Gude, Mannarswamy, Cooke, et al., 2011). This in turn lowers the activation energy of the reactant thereby accelerating the forward reaction (Zabeti, Wan Daud, and Aroua 2009). (Patil, Gude, Mannarswamy, Cooke, et al., 2011). On the other hand, ultrasound induces intense mixing due to continuous compression and rarefaction cycles which causes cavitation bubbles (Martinez-Guerra et al., 2014). This generates super high local temperatures and pressures thereby increasing bulk temperature and reactant interaction, thus accelerating the reaction (Suganya, Kasirajan and Renganathan, 2014). These two processes can also be used one after another and even in combination.

The transesterification process is also driven by a strong catalyst (Bharathiraja et al. 2014). Esterification and transesterification processes take time to be completed without a catalyst and the process is also reversible. The catalysts used are either homogenous acid, homogenous base, heterogeneous acid, or heterogeneous base. Acid catalysts had been known to be more efficient since it does not yield soaps, however they are corrosive and toxic (Ehimen, Sun, and Carrington 2010). Homogenous catalysts are popular but they could not be reused and separating them after transesterification has become an issue (Liu et al. 2008). Heterogeneous catalysts solves the separation issue but they are a bit more expensive and it tends to lengthen the reaction process (Zabeti, Wan Daud, and Aroua 2009). This study proposes the use of a heterogeneous alkali catalyst that is easy to prepare, cheap,

and can give relatively high FAME yield of biodiesel from waste vegetable oil.

## II. MATERIALS AND METHODS

### A. Materials

The waste vegetable oil used in these study where by-products of a known fast food chain in Roxas City. The waste vegetable oil were purchased and delivered in regular plastic white gallons. The oyster shells used in the study where sourced in nearby restaurants serving oyster shell meats. Other materials necessary in the oil extraction, transesterification and analysis of biodiesel were purchased at stored located in Iloilo City, Phillipines. The microwave used in the study was purchased at a commercial store in Roxas City, Capiz. The microwave had a maximum output power of 1000 watts.

### B. Preparation of Catalyst

Oyster shells retrieved from restaurants where first boiled for an hours to eliminate pathogens and unnecessary smell. The shells were then sundried to eliminate moisture. The dried oyster shell where then powdered using mortar and pestle. Powdered oyster shell material was then placed in an oven for 3 hours at 120°C to further eliminate moisture. It was then ion exchanged with different NaOH solutions for 24 hours to impregnate the sodium ions. The mixture was then filtered to separate the powder where it was placed again in the oven at 120 °C for another 3 hours. The subsequent product is placed in a desiccator to let cool for a few hours and was later transferred to a dry jar for storage.

### C. Catalyst Characterization

Sodium impregnated oyster shells characterized using Hammett indicators and X-ray Diffraction (XRD). The Hammett Indicators measured base strength of the catalysts and its base total amount. The base strength is measured with pH of aqueous solution saturated with catalyst (20g / 50 ml). Base total amount was measured by titrating 0.1N Benzoic Acid in Benzene to the mixture of 1g catalyst sample in 20ml Benzene with 1 ml indicator solution (phenolphthalein in ethyl alcohol).

The XRD was performed using the Bruker D8 Advance ECO equipment. First, the sample was placed in the sample holder of a two circle goniometer, enclosed in a radiation safety enclosure. The X-ray source was a 1kW Cu X-ray tube, maintained at an operating current of 40 kV and 25 mA. The X-ray optics was the standard Bragg-Brentano para-focusing mode with the X-ray diverging from a DS slit (1mm) at the tube to strike the sample and then converging at a position sensitive X-ray Detector (Lynx-Eye, Bruker-AXS). The software suit for data collection and evaluation is windows based. Data collection is automated COMMANDER program by employing a DQL file. Data is analyzed by the program EVA. The IR measurements were performed with the Shimadzu IR Affinity-1 equipment. The KBr pellet technique was used in determining IR spectra of the samples at room temperature. The range was adjusted at 600–4500 cm<sup>-1</sup>, with 300 scans and 4 cm<sup>-1</sup> resolution.

### D. Transesterification Reaction

A gallon of waste vegetable oil was bleached, degummed, and dewaxed according to the procedure described by L. Rajam, et al. Fifty grams of the refined waste vegetable oil was then weighed and placed in a 250ml flask. Methanol and sodium loaded catalyst was then added to the same flask before it is placed in the reaction vessel and into the microwave oven. The amount of methanol (from 6:1 to 22:1 methanol to oil ratio) and catalyst (2 to 20% by weight of oil) were varied during every experiment. The transesterification process starts as soon as the microwave is turned on and the length of the reaction was varied on each experiments (1 – 20 min). The output power of the microwave was varied as well from 200 to 1000 watts. The variations for the process parameters were done to identify the optimum values of each during these experiments. During ultrasound transesterification experiments, the reaction starts as soon the sonicator was turned on and the ultrasonic frequency was varied from every experiments.

At the end of these experiments, the catalyst was recovered from the reaction mixture by filtration. The filtrate was then placed in the rotary evaporator to free the mixture from unreacted methanol. The mixture was then placed in a separatory funnel and let stand for 6 hours. The glycerine that sank at the bottom was removed and the remaining biodiesel was washed with 20% hot water by weight to dissolve soap. The water with dissolved soap settles at the bottom of the flask and was drained in the separatory funnel. The remaining product which is the biodiesel is then weighed and a sample was loaded and analysed by the GC-MS.

The separated catalyst was washed with methanol, dried and calcined for 12 hours in a temperature of 300 °C. It was again regenerated by ion exchanging in a 1.0 N NaOH aqueous solution and placed in a 120 °C for 3 hours. The catalyst was then transferred to a desiccant to cool where it was then placed in a clean dry jar.

### E. Analysis

The fatty acid methyl ester (FAME) composition in the final product was analysed by GC-MS. The samples were dissolved in dichloromethane in the ratio 1:4 and placed into the GC tray. Helium was the carrier gas and the sample's injection volume was 1.0 µl at a temperature equal to 180 °C. The temperature program of the GC-MS was set at 50 °C held for 5 min, increased to 250 °C at 5 °C/min, and held at 250 °C for another 10 minutes. Methyl stearate was used as the standard to determine the relative weight composition of the sample. The biodiesel's FAME yield was calculated by its weight in the crude biodiesel relative to the weight of raw waste vegetable oil.

## III. RESULTS AND DISCUSSION

### A. Catalyst Characterization

The Hammett Basicity Test conformed the highly basic properties of the synthesized catalyst. Sodium loaded oyster shell at 2.0N solution had a base strength measured at 12.5 and the base total amount was 55 mmol/g. This is a significant

improvement that should increase the catalytic properties of the synthesized catalyst from the original material. Table 1 shows the difference of the base total amount and basicity of oyster shells powder loaded at different NaOH concentrations.

The XRD pattern of the blank pumice (Figure 1) highlighted two peaks that suggested the presence of silica and paragonite quartz. The two are the most common crystalline substance in the surface of the oyster shell powder. By

impregnating it with sodium ions (Figure 1), XRD had revealed the formation of other crystals as well.

TABLE 1. Base strength and base total amount of Oyster Shell Catalyst

Material	Base Strength	Base total amount (mmol/g)
Pristine Oyster Shell	8.7	8
0.5 N Na- Oyster Shell	11.7	33
1.0 N Na- Oyster Shell	12.4	51
2.0 N Na- Oyster Shell	12.5	55

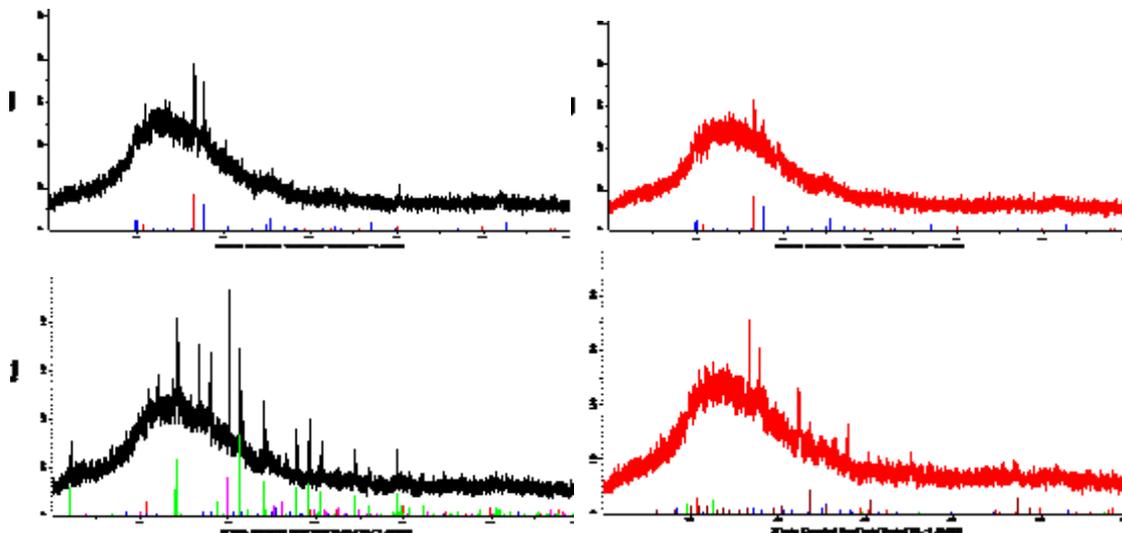


Fig. 1. Clockwise from upper left: XRD patterns of Pristine Oyster Shell, 0.5 N Na- Oyster Shell, 1.0 N Na- Oyster Shell, 2.0 N Na- Oyster Shell

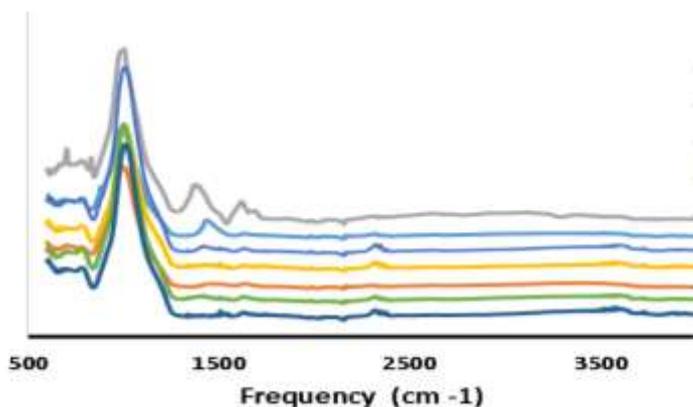


Fig. 1. FTIR of pumice and selected synthesized catalysts

### B. Transesterification Process

The transesterification experiments were done to investigate if the synthesized catalyst would be a better alternative in the production of biodiesel from microalgae. Another objective is to determine the process parameters that would have the best FAME Yield. The first experimental runs were aimed to answer what would be the ideal output power that is to be set in the microwave. Consequently, it also answered what is the time the best FAME yield is achieved. In order to determine this, the other process parameters were fixed first. The basis of the values of the these parameters prior to the investigation of the first variable to be tested were the optimum parameters described in transesterification

studies involving solid alkali catalysts(Lam, Lee, and Mohamed 2010). These process parameters were identified to be methanol to oil ratio at 18:1 and catalyst load at 10%.

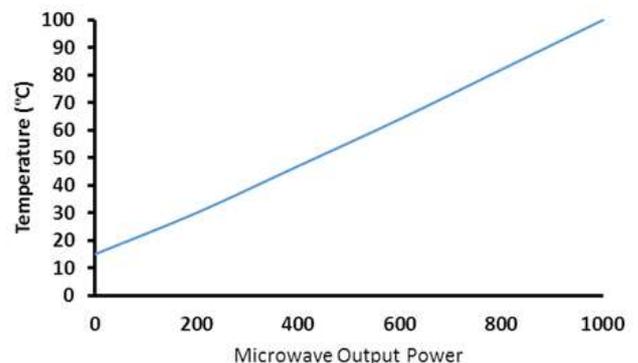


Fig. 3. Reaction temperature of the mixture at different Microwave Output Power

The process parameters that are usually investigated in transesterification procedures are methanol to oil ratio, catalyst loading, reaction time, and reaction temperature. Instead of reaction temperature however, it would be the microwave output power that will be presented. Not only does microwave output power translate to reaction temperature (Figure), but also a specific temperature can hardly be set in a regular microwave oven. Also, to simplify the data that will be presented in this section and the succeeding one, the

synthesized catalyst impregnated in 1.0N solution will be used. The previous work had already proven that optimum contact solution for catalyst synthesis is 1.0N.

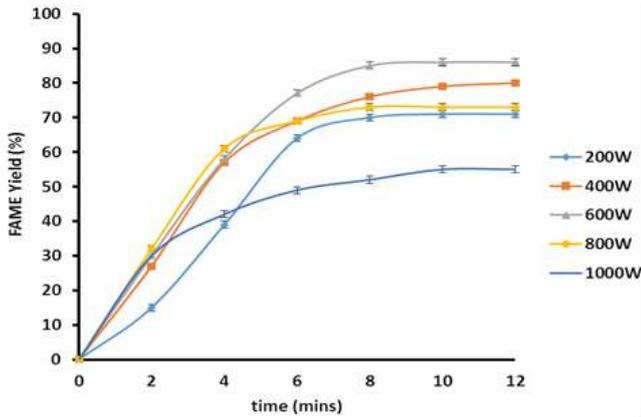


Fig. 4. FAME Yield vs reaction time at different microwave output power

In the investigation of the optimum microwave power using Oyster shell as the catalyst (Figure), it was found out that the best FAME yield was achieved when the output power was 800 Watts. The second highest output was achieved when microwave power was set at 600 Watts. As based upon the graph presented in Figure, it can be shown that the reaction temperature of the mixture are 64 °C and 45 °C respectively. This means that setting the microwave power beyond 600 Watts will increase the temperature of the mixture beyond the boiling point of methanol. By doing this, the methanol to oil ratio will be lowered drastically thereby affecting the FAME yield of the biodiesel negatively. Consequently, the optimum reaction temperature was also identified in the investigation of microwave output power. It is noted that the reaction is already completed achieving a FAME yield of 80% just after 15 minutes when the microwave output power was set at 800 Watts and the catalyst used was oyster shell powder impregnated at 1.0N NaOH solution.

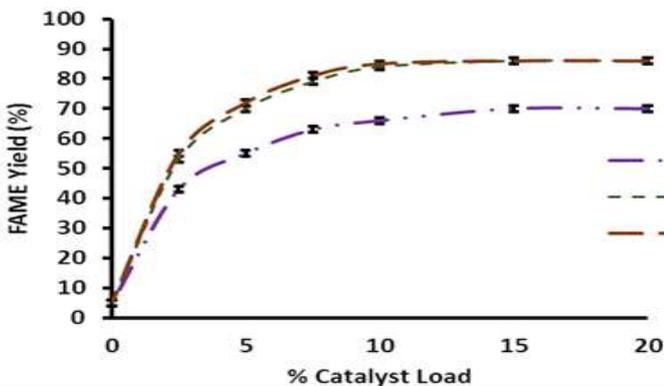


Fig. 5. Influence of catalyst load on the FAME Yield of the microwave-assisted transesterification using the synthesized catalysts

When the reaction time and microwave output power was already optimized, the two remaining process parameters must also be investigated. The optimum reaction time and microwave output power was used in order to determine the

best catalyst load. By setting the output power at 800 watts, reaction time to 15 minutes, and methanol to oil ratio to 18:1, it was identified that the catalyst load capable of achieving the highest FAME yield possible is at 20%. The FAME yield identified at this percentage was 80%.

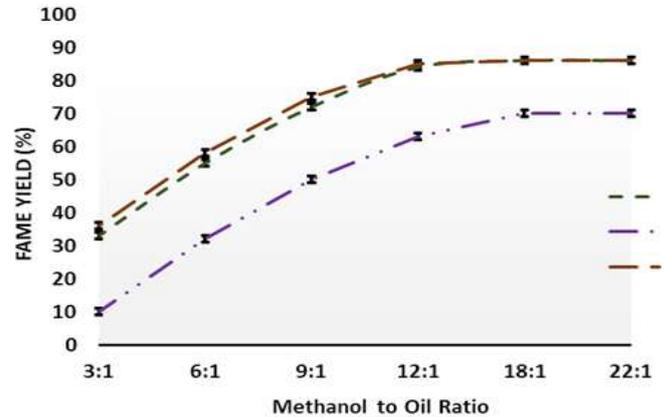


Fig. 6. Influence of methanol to oil ratio on the FAME Yield of the microwave-assisted transesterification using the synthesized catalysts

By setting the catalyst load at 20%, reaction time at 15 minutes, and microwave reaction power at 800 Watts, it was identified that the optimum methanol to oil ratio was 15:1. It means that a lesser amount of alcohol will be needed to produce biodiesel with even a better FAME yield. Economically speaking, lesser alcohol needed means cheaper biodiesel produced.

#### IV. CONCLUSION

Sodium loaded oyster shell powder was synthesized by ion exchanging it with 1.0N NaOH solution. It was able to generate up to 80% FAME yield during transesterification reactions using waste vegetable oil and with the assistance of microwave. The materials needed for synthesis are cheap and easy to find. It was also easy to prepare and can be separated by filtration making it a viable alternative catalyst in biodiesel production. The optimum methanol to oil ratio = 15:1 and catalyst load = 20%. Optimum reaction time for ultrasound-assisted transesterification was 20 minutes at ultrasonic percent amplitude of 40%. Optimum reaction time for microwave-assisted transesterification was 15 minutes at microwave output power of 600 watts.

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