Analysis of Engine Emissions from Biodiesel Prepared by Using Calcined Egg Shell Powder as a Heterogeneous Catalyst

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Abstract

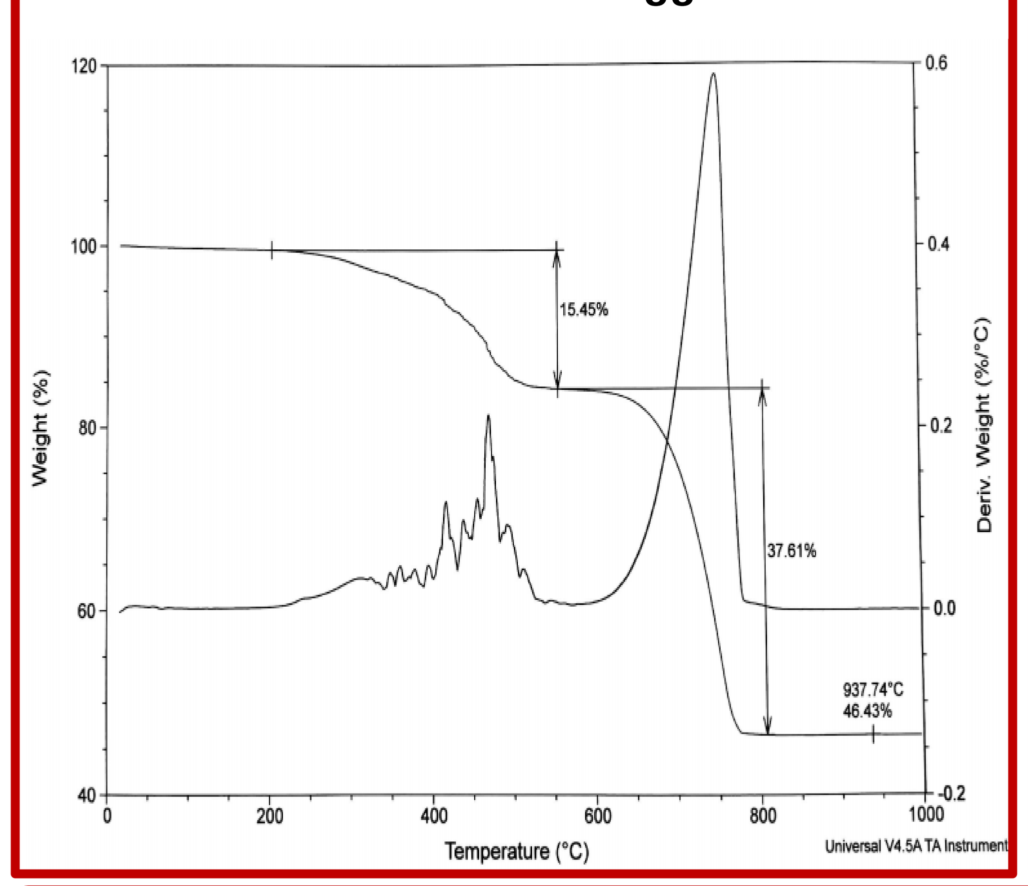
Egg shells were calcined at 1000℃ for 4 hours to obtain calcium oxide (CaO) which was investigated as a heterogeneous catalyst for the transesterification of waste cooking oil. The catalyst was characterized by Fourier Transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). Process parameters such as methanol-to-oil molar ratio, catalyst concentration, and reaction time on biodiesel yield were all evaluated and optimized. A maximum biodiesel conversion of 99.11% was obtained at 9:1 methanol to oil molar ratio, 4 wt.% catalyst loading, 2 hours of reaction time, and reaction temperature at 65℃. The percentage conversion was determined by ^{1}H NMR. Additionally, the biodiesel synthesized was subjected to treatment methods including the hydrogenation of the double bonds in the FAME which are responsible for fuel gelling at low temperatures. The emission profile for various combinations of the biodiesel produced and the ultra-low sulfur petroleum diesel in a diesel-powered generator was characterized by gas chromatography coupled to mass spectrometry (GC-MS) and FTIR. The fuel mixture with 30% biodiesel blend was found to yield the lowest levels of carbon monoxide, methane, ethylene, and formaldehyde.

Materials & Methods

- Egg shells were washed and calcined at 1000 ℃ in a muffle furnace for 4 hours.
- The calcined egg shell was characterized by FTIR and TGA
- It was utilized as a heterogeneous base catalyst for the transesterification of waste cooking oil and methanol.
- Excess methanol was distilled and percentage conversion of the pure biodiesel determined by ^{1}H NMR.
- The biodiesel was blended with Ultra Low Sulfur Petroleum Diesel (ULSPD) in different proportions and used in a diesel-powered generator.
- The emission was collected for different biodiesel/petroleum diesel blends in a Tedlar bag and analyzed by FTIR and GC-MS

Catalyst Preparation Conditions

TGA Curves of Uncalcined Egg Shell Powder.

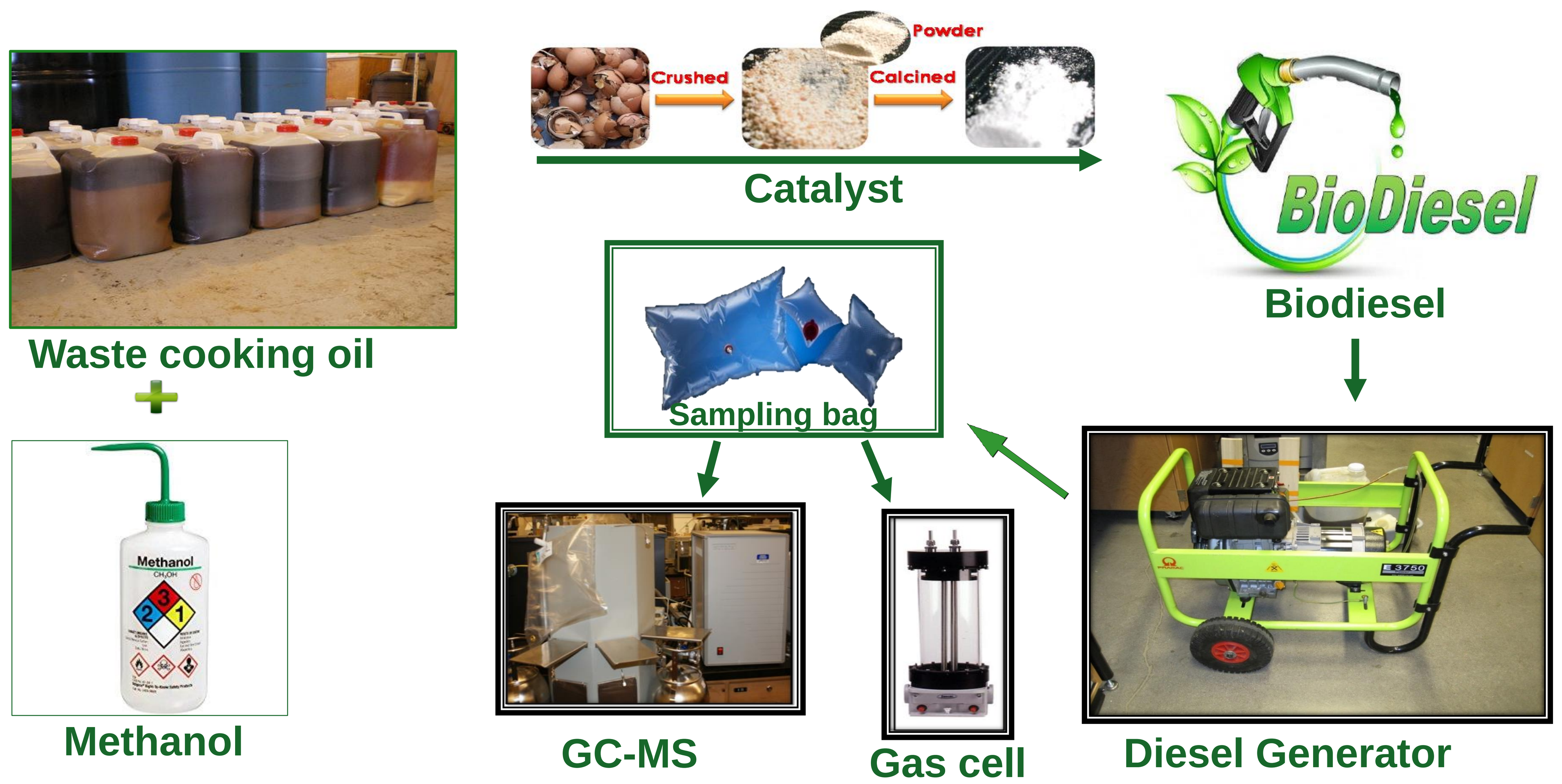


- The TGA curve shows the decomposition temperature of ground egg shells when heated in a controlled environment.
- A two-stage weight loss was observed. The weight loss at 0−565℃ is attributed to loss of surface water and organic impurities present in the shell powder.
- At the temperature range of 525-800 ℃, a significant weight loss was observed due to the release of carbon dioxide from the decomposed calcium carbonate.

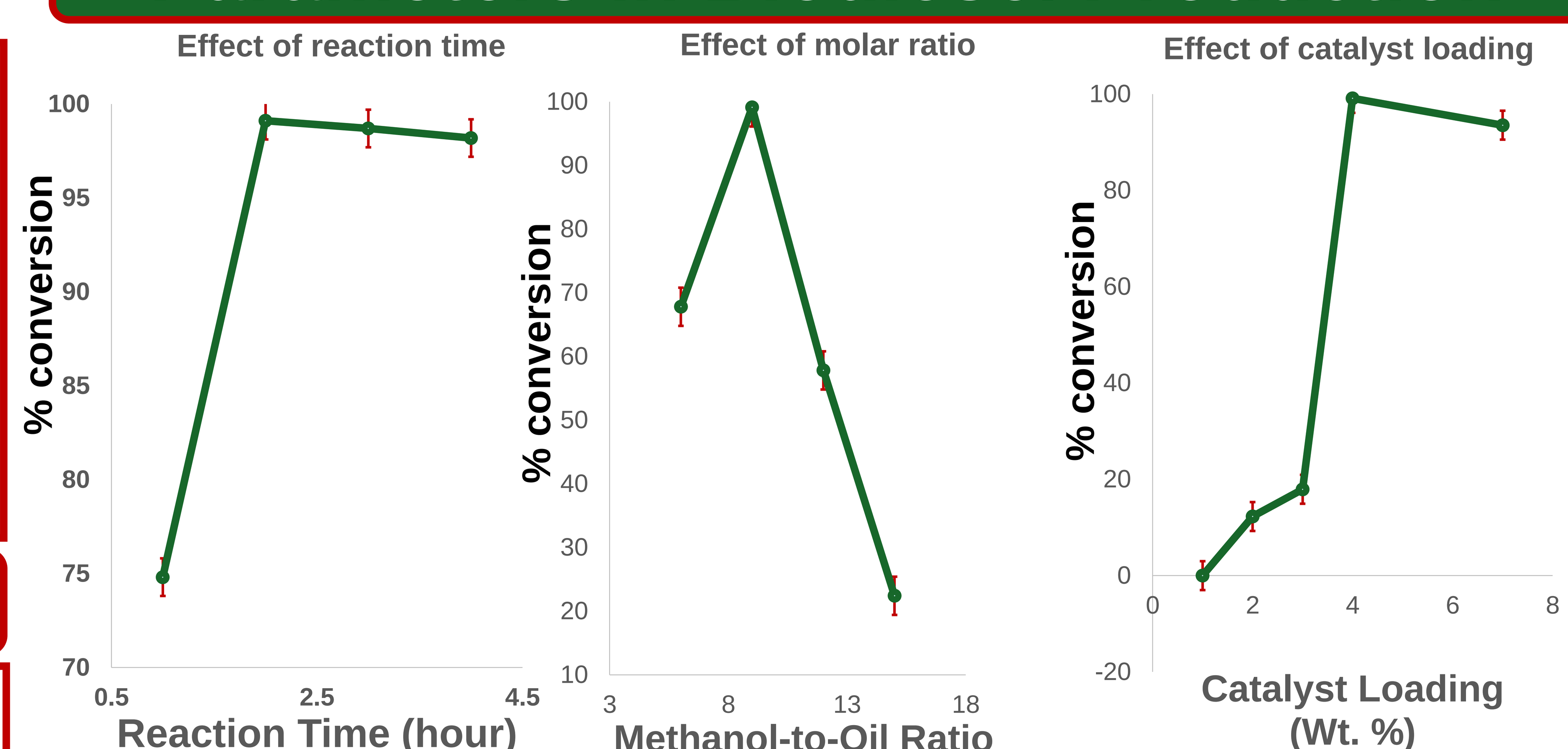
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

- At above 800 ℃, the sample weight remained constant which is indicative of complete decomposition to CaO.
- The calcination temperature should be above 800 ℃ to ensure the complete conversion of the egg shell to CaO.

Summary of Work in Pictures



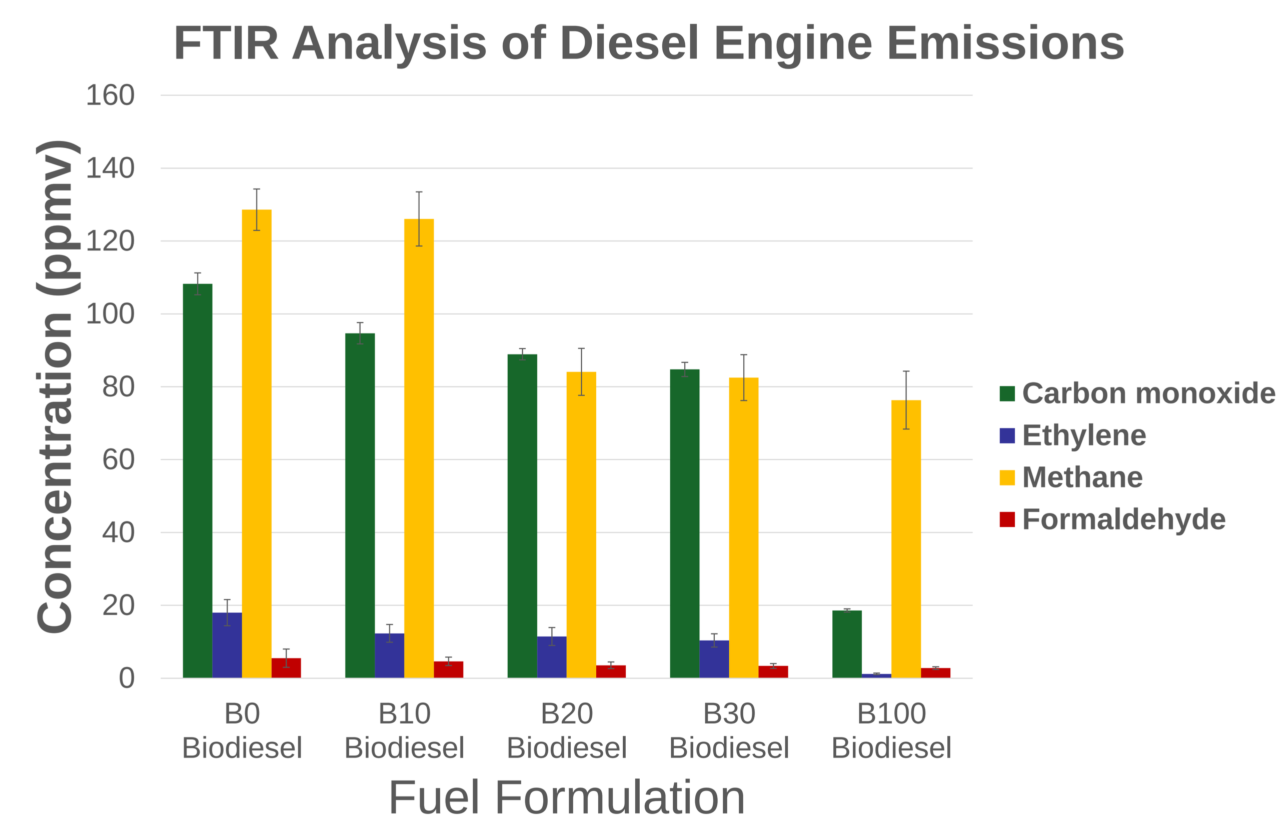
Parameters in Biodiesel Production

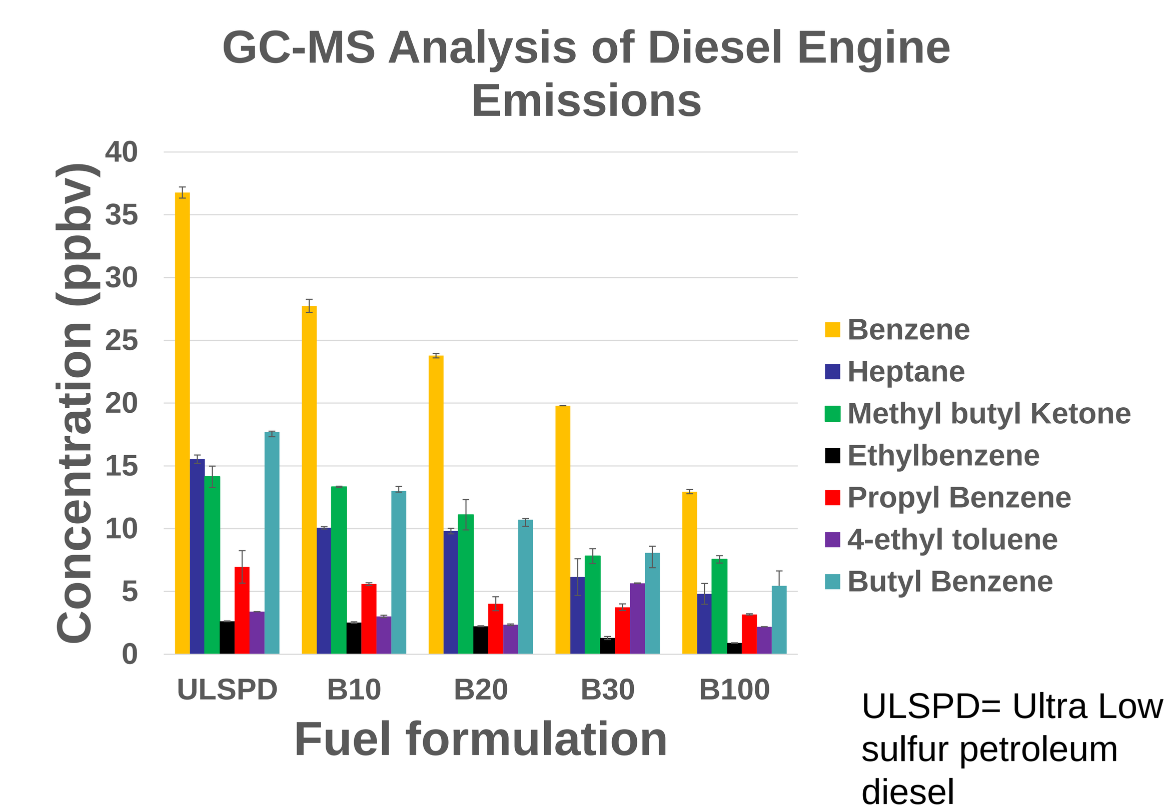


Results and Discussion

- **Reaction time:** The observed trend is due to increased product yield via transesterification as time progresses; this is then followed by soap formation beyond 2 hours of reaction time which led to the loss of ester.
- **Catalyst loading**: The trend shown is due to increased contact surface at higher catalyst loading of up to 4 wt. % when additional catalyst promotes an equilibrium shift toward saponification reaction and therefore causes the reduction in yield.
- **Methanol-to-oil molar ratio**: Excess alcohol is needed to shift the equilibrium toward biodiesel production at up to the optimal methanol-to-oil ratio of 9: 1. Beyond that, the biodiesel ester yield began to decrease.
- In emission testing with the diesel-powered generator, the concentration of the VOCs decreases with increasing biodiesel concentration blended into petrodiesel.

Fuel Emission Profiles





ULSPD= Ultra Low sulfur petroleum diesel

Conclusion

- A heterogeneous base catalyst was obtained from egg shell by calcination.
- The calcined egg shell exhibited excellent catalytic activity towards transesterification of waste cooking oil and methanol yielding a percentage conversion as high as 99.1%
- The optimum reaction condition was 9:1 methanol to oil molar ratio, 4 wt.% catalyst loading, 2 hours of reaction time, and reaction temperature at 65℃
- The highly efficient and low-cost egg shell catalyst could make the process of biodiesel production more cost-effective and environmentally friendly.
- The optimal biodiesel-petroldiesel blend percentage is related to cost of production and emission profiles.