



Development of Functional Carbon Nanotubes as Catalyst for Biodiesel Production

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Abstract: The main objective of this study is to develop carbon-based catalysts as applied to the conversion of biomass to value-added chemicals and biofuels focusing on microalgae, marine and non-edible biomass resources as feedstocks. Specifically, carbon nanotubes (CNTs) chemically modified with sulfonic or amine groups to adjust its acidity or basicity, respectively will be developed. Functional CNTs will then be applied to reaction systems using environmentally friendly microwave and supercritical fluid technologies. Preliminary results showed the successful production of carbon nanotubes (CNT) via chemical vapor deposition- microwave enhanced process. CNTs were also successfully modified using sulfonate and amide groups. Further, supercritical fluid catalytic reactor using CO₂ also modified the structure of CNTs.

Key Words: Carbon nanotubes; microwave and supercritical fluid technologies; biodiesel production.

1. INTRODUCTION

1.1 CNTs as Catalyst for Biodiesel Production

Carbon nanotubes (CNTs) are probably the most well known of nanomaterials. These materials have an interesting class of nanostructure thereby attracted great attention due to their outstanding properties and potential applications. CNTs consists of tubes of graphite-like material closed in on itself to form cylinders with diameters ranging from ~ 1nm up to several nanometers but with length that can approach millimeters or more (Lindsay, 2010). The three (3) widely used methods for CNT production are arc discharge, laser ablation, and chemical vapor deposition (CVD) methods. Recently, CVD method is commonly used to produce both single-walled and

multi-walled CNTs. Plasma enhanced CVD is a novel technology that improved the deposition method due to the presence of charge species and radicals under the electronic field.

Meanwhile, base catalysts are not suitable in biodiesel production due to inevitable saponification reaction between catalyst and FFA to form soaps. It consumes the catalyst and requires expensive separation steps downstream to purify the biodiesel. Hence, the use of acid based catalyst draws a lot of attention to researchers. Most studies conducted in biodiesel production used sulfonic based catalyst to form active acid sites. Sulfonic acid catalyst can be homogeneous and heterogeneous catalyst for biodiesel production. One of the advantages of using heterogeneous catalyst is its reusability in transesterification process (Rubio, 2010).



2. METHODOLOGY

PRODUCTION OF CNT

In this study, CNTs were produced via chemical vapor deposition- microwave enhanced process. A metallic washer was used as substrate for the catalyst. Nickel thin film was employed as the source for nanoparticle catalyst. It uses acetylene as carbon source and pencil lead made from graphite as emitter. A Whirlpool AVM-585 domestic microwave oven was used in this experiment with an input power of 1,350 W and magnetron output power of 850 W. The reactor was made from quartz glass that can withstand high temperatures. Photos of microwave set up and reactor are shown in **Figure 1**.



A



B

Fig. 1. Photos of (A) Microwave set up and (B) Reactor

On the other hand, the schematic diagram of the high pressure catalytic reactor system used in this study is presented in **Figure 2**. In this set up, liquid CO₂ is delivered to liquid CO₂ pump which compressed the liquid CO₂ to above critical pressure. The CO₂ is then delivered to a stainless steel coil which is placed in a temperature controlled oven. The temperature of this oven is maintained at 40°C which is above the critical temperature of CO₂. This supercritical fluid is then delivered to the high pressure reactor, which is also located inside the temperature controlled oven where extraction and reaction could be done simultaneously.

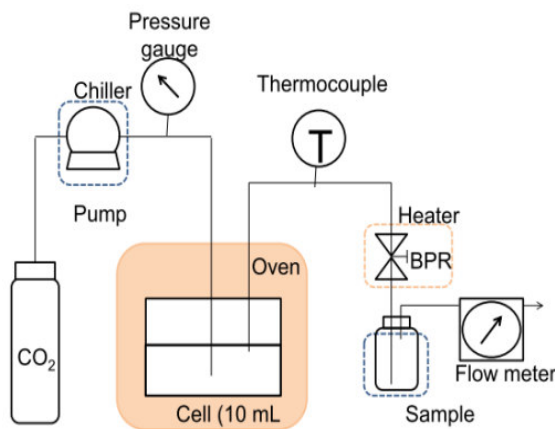


Fig. 2. Schematic Diagram of High Pressure Catalytic Reactor System

Modified CNTs were characterized using BET, SEM-EDX and FTIR.

PURIFICATION OF CNT

Prior to functionalization, carbon nanotubes were purified by acid washing or by sonication, a technique that permits separating the nanotubes from amorphous carbon and metallic catalysts impurities. In addition, this procedure induces the incorporation of -COOH and -OH groups, which bind

to the CNTs at the end termini and/or the sidewall defect sites.

The carbon nanotube was purified prior to addition of amine or sulfonic groups. The modified procedure of Shuit and Tan (2014) was used in the experiment. A mixture of pristine 0.1 g of multiwalled carbon nanotubes and 50 mL HCl was subjected to 2 hours of ultrasonication treatment for 80 °C. The treated carbon nanotubes was filtered, washed with distilled water until the pH of the filtrate is the same as the pH of the distilled water. It was dried at 120 °C for 2 h to obtain MWCNT-COOH.

SULFONATION OF CNT

Sulfonation of carbon nanotube was prepared based on the modified experimental details reported by Yu et al (2008) on the synthesis and characterization of a sulfonated single walled carbon nanotube as solid acid catalyst. A 100 mg of CNT was mixed in a dry flask at 50 mL concentrated H₂SO₄ (98%). It was sonicated for 30 mins, followed by heating to 120 °C in an metal plate under fume hood for 3 hours. The suspension was diluted by water and filtered. The solids were washed to remove excess acid. Finally, carbon nanotubes were dried at 120 °C to obtain sulfonated carbon nanotube.

AMIDATION OF CNT

Similar procedure to sulfonation was used in the addition of amide group to carbon nanotube. Below is the detailed procedure of amidation process. A 100 mg of CNT was mixed in a dry flask at 50 mL monoethanolamine. The mixture was sonicated for 30 mins, followed by heating to 120 °C in an metal plate under fume hood for 3 hours.

The suspension was diluted by water and filtered. The solids were washed to remove excess acid. Carbon nanotubes were dried at 120 °C to obtain amidated carbon nanotube.

3. RESULTS AND DISCUSSION

Preliminary results showed that SEM micrograph of the laboratory produced CNTs as depicted in **Figure 3** are similar to that of the commercial CNT. As observed, CNT strands of both samples have similar diameters.

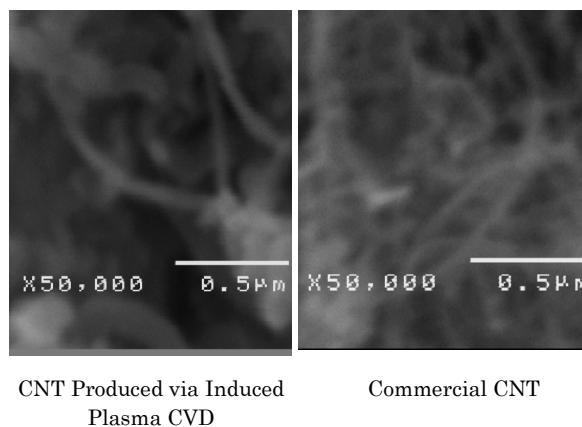


Fig. 3. SEM Micrographs of CNTs

The EDX result of CNTs produced as presented in **Figure 4** shows the presence of contaminants Ni and O. The presence of contaminant O can be ascribed to the oxidation of transition metals present in CNTs forming metal oxides. Nickel came from the catalyst deposited on the Fe substrate so that CNT can form when the feed gases are in plasma state.

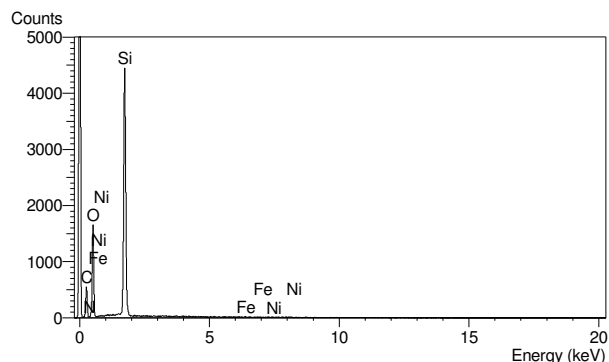


Fig. 4. EDX Analysis Result of CNTs

The FTIR spectra of pristine multiwalled carbon nanotubes (A) and sulfonated multiwalled carbon nanotubes (B) in the region from 4000 to 400 cm^{-1} are presented in **Figure 5**.

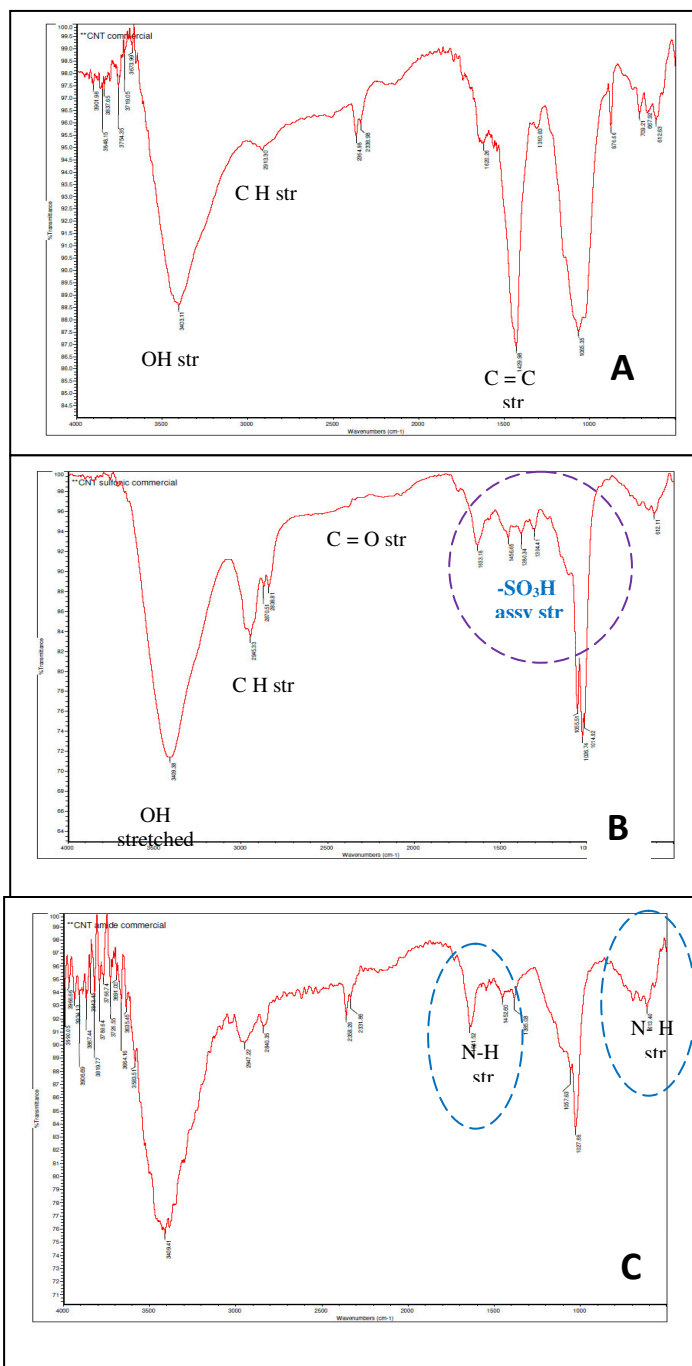


Fig. 5. FTIR Spectra of (a) pristine CNT (b) sulfonated CNT and (c) amidated CNT

Based on FTIR results, CNTs were successfully modified using sulfonate and amide groups. In the spectrum of p-MWCNTs, there exist important absorption bands of OH moieties and/or OH in carboxyl groups and absorbed water, alkane stretch CH, C=O stretch, and SO_3H at 1245 -1155 cm^{-1} range. The new representative absorption peaks indicate that sulfonic acid groups were successfully grafted onto the surface of MWCNTs by this method.

Meanwhile, supercritical fluid catalytic reactor using CO_2 also modified the structure of CNTs by bloating the tubes thereby increasing the diameters of CNTs. **Figure 6** shows the SEM images of CNTs modified using high pressure catalytic reactor. The supercritical fluid catalytic reactor using CO_2 may have modified the structure of CNTs. It could be observed that the diameters of both samples increased. The subcritical CO_2 may have penetrated through the multiwalls of the CNT during pressurization and when the pressure is released, the CO_2 expands thereby bloating the tubes. These results will be further investigated. The attachment of the carbonyl group into the walls will be examined by FTIR and SEM EDX.

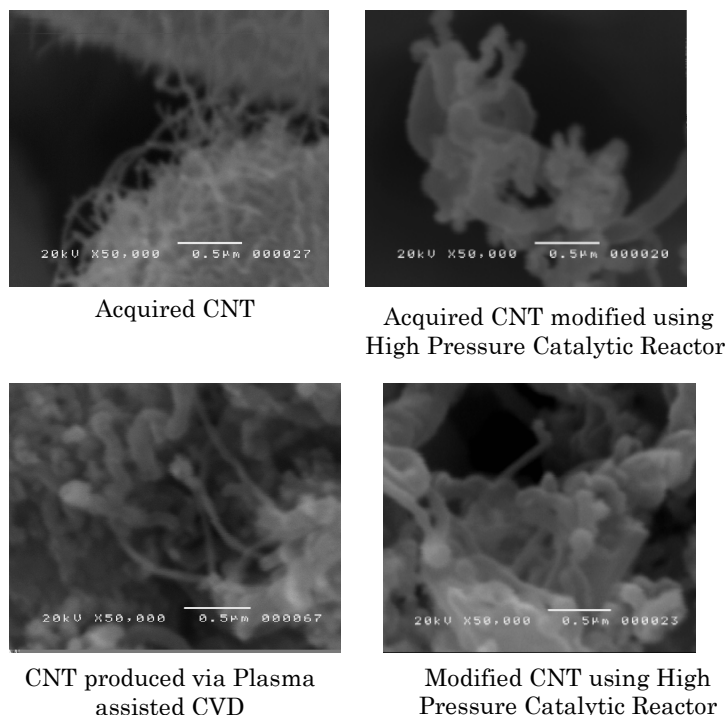


Fig. 6. SEM images of Acquired CNT and modified using High Pressure Catalytic Reactor



4. CONCLUSIONS

Preliminary results showed successful production of carbon nanotubes (CNT) via chemical vapor deposition- microwave enhanced process. CNTs produced were successfully modified using sulfonate and amide groups. Supercritical fluid catalytic reactor using CO₂ can also be used to modify the structure of CNTs.

5. ACKNOWLEDGMENTS

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