

Supercritical Water Gasification of Vegetable Oil Using Nickel Catalyst

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1. Introduction

Supercritical water gasification (SCWG) is an innovative biomass conversion technology that has been receiving a lot of attention from the research community. This process utilizes the unique properties of supercritical water ($T > 374$ °C and $P > 22.1$ MPa) that enables the transformation of biomass into H_2 -rich gaseous products. Current research on SCWG focuses on how to reduce the operating cost and equipment investment. One available option to meet the high temperature and pressure requirements is to reduce the activation energy by adding suitable hydrothermal catalyst. However, the efficiency of this process is currently limited by catalyst deactivation. While catalyst deactivation is inevitable, most of its consequences may be slowed down or avoided. Understanding the catalyst behavior during the SCWG gives the knowledge of how process parameters influence its catalytic performance, thereby enhancing its efficiency. From the viewpoint of food sustainability, the utilization of non-food biomass such as waste vegetable oil is recommended. In Japan, the amount of cooking oil consumed in FY2008 came to 2.27 MT. Of this, as much as 0.06 – 0.08 MT of vegetable oil from the food service industry and 0.09–0.1 MT from ordinary households go unused^[1]. In Philippines, large amounts of vegetable oil are illegally dumped into rivers and landfills causing environmental pollution. Its disposal problem is also observed in other parts of the world, particularly in developing countries^[2]. Its known treatment method is conversion to 2nd generation biodiesel through the process of transesterification and hydrodeoxygenation. However, these methods have disadvantages which often result in low product conversion and hydrogen efficiency. Utilizing vegetable oils can be a good potential in H_2 production using supercritical water gasification. This study has two main objectives. First, it aims to study the applicability of SCWG in vegetable oil treatment. Second, it aims to observe the behavior of nickel catalyst during supercritical water gasification of vegetable oil.

2. Methodology

The representative vegetable oil biomass used in this study was canola oil. It is mainly composed of C (77.51%), H (11.62%) and O (10.87%) as determined by CHN analysis. Two types of pumps were used to deliver the reactants to the system. Slurry and plunger pumps were used to deliver water and oil, respectively. The catalyst used in the study was composed of Ni (67.2%), Al (31.9%), and Mo (0.9%) with an average BET surface area of $58.23 \text{ m}^2 \text{ g}^{-1}$ and was purchased from Nikko Rica, Japan. The laboratory-scale flow system was made of stainless steel (SUS 316) tubing and Swagelok® SUS 316 fittings/valves. The cylindrical furnace with temperature set to 700 °C was used to heat and maintain the temperature of both preheater and reactor at 400 °C. The system was pressurized at 25 MPa. Figure 1 presents the schematic diagram of the system. The amount of total organic carbon (TOC) present in the liquid phase was determined using TOC-V. The organic compounds dissolved in the liquid phase were also analyzed using GC-MS and HPLC. The amount of heavy metals eluted to the liquid phase was analyzed using ICP-MS. Gas phase analysis was performed using GC-TCD to separate H_2 , CH_4 , CO , and CO_2 . Catalyst characterization before and after the reaction was carried out using N_2 adsorption/desorption techniques performed with Gas Sorption System, NOVA 2000e. To determine the change of catalyst crystal structure, XRD was employed. To probe the catalyst surface and quantify the existing elements on its surface, SEM-EDX analysis was carried out.

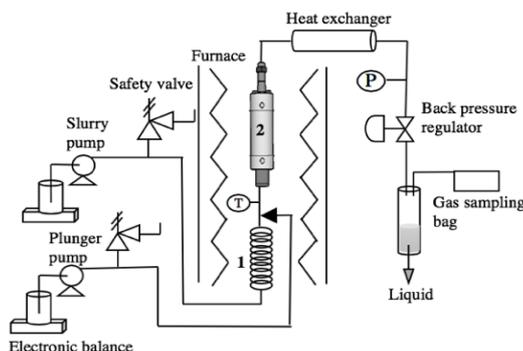


Figure 1. Schematic diagram of the SCWG system used in the study. (1) Preheater (2) Reactor

3. Results and Discussion

3.1. Decomposition of oil in SCWG

The decomposition of oil in supercritical water gasification has been studied. The experiments were conducted to evaluate the effect of biomass concentration using four (4) different oil concentrations, herein denoted as SCWG 0.02, SCWG 0.03, SCWG 0.04, and SCWG 0.05, representing 2%, 3%, 4% and 5% oil concentration in water respectively. All experiments were conducted at 400 °C, 25 MPa and reactor residence time of 4.5 s. The efficiency of the process was evaluated according to gas yields and efficiencies. Figures 2 and 3 show the results obtained for the SCWG of 2% and 5% oil concentration.

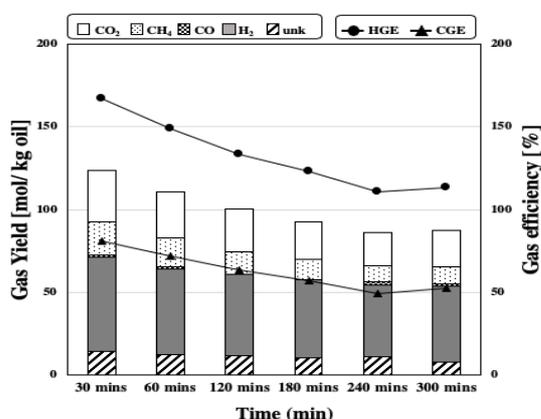


Figure 2. Gas yield and efficiency of SCWG 0.02 at 400 °C, 25 MPa and 4.5 s residence time.

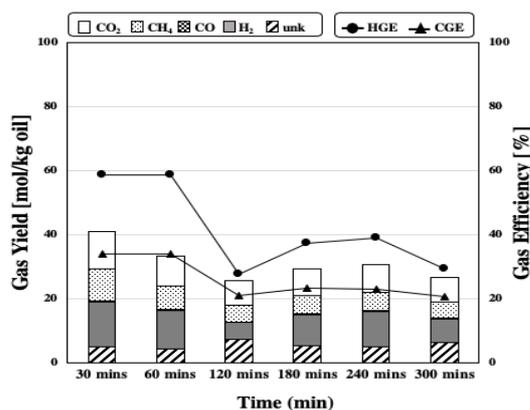


Figure 3. Gas yield and efficiency of SCWG 0.05 at 400 °C, 25 MPa and 4.5 s residence time.

In Figure 2, the process was able to achieve high gas yields, especially H₂ yield. The HGE also reached more than 100%. To clarify whether this high H₂ yields were contributed by H₂ present in the catalyst pores, a blank test was added using pure water only and 10%

catalyst amount. The H₂ gas yield is only 0.15 mol/kg H₂O refuting our assumption. Instead, H₂ could have come from the biomass. The results showed that all experimental condition followed the same pattern in terms of gas yields and efficiencies. During the initial phase of the reaction, high gas yields and efficiencies could be observed; however, this was followed by a steep decline of both performance parameters. It was also observed that gas yield decreases as oil concentration increases. From a study by Yu et al.^[3], they also found this similar trend. From their results, the yields of H₂ decrease while CH₄ yield increases as

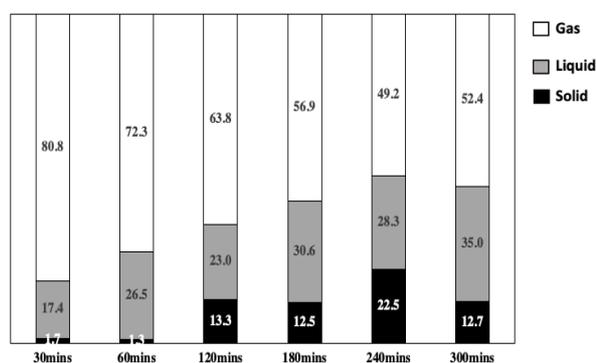


Figure 4. Carbon balance for SCWG 0.02.

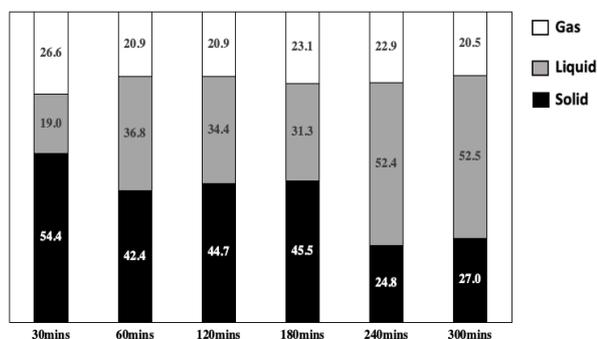


Figure 5. Carbon balance for SCWG 0.05.

glucose concentration increases. The appearance of unknown gas products is also observed. According to Nguyen et al.^[4], these 'unknown' gases are thought to be C₂-C₄ hydrocarbons. From this study, both H₂ and CH₄ yields decreased while the production of C₂-C₄ hydrocarbons increase as oil concentration increases. The appearance of these C₂-C₄ hydrocarbons is possibly connected with catalyst deactivation. One possibility for the appearance of these C₂-C₄

hydrocarbon molecules is that they were produced in the earlier part of the reaction due to breakdown of larger molecules. These molecules then appear in the product gas stream without undergoing the complete steam reforming process and this may be due to the insufficient activity of the catalyst. Examining the carbon balance, the increase in the solid proportion is notable suggesting that organics such as char or tar may have been formed. Thus, the presence of C₂-C₄ hydrocarbon may be correlated with incomplete feed conversion. Assuming that a spectrum of molecules is produced during the initial phase of the reaction, highly active catalysts that give close to 90 – 100% carbon conversion, would have converted all C₂-C₄ hydrocarbons to C₁ molecules. However, from Figures 2 and 3, it is evident that catalytic activity is insufficient or as catalyst efficiency declined, these broken hydrocarbons passed through the catalyst bed without undergoing complete steam reforming. This proves that catalyst deactivation behavior can be observed with the system's ability to convert the carbon present in the biomass. It is also concluded that at lower biomass concentration, the system performance is comparably better than higher biomass concentration. Therefore, through system optimization, SCWG can be a promising process in gasifying and converting vegetable oil into desired gaseous products.

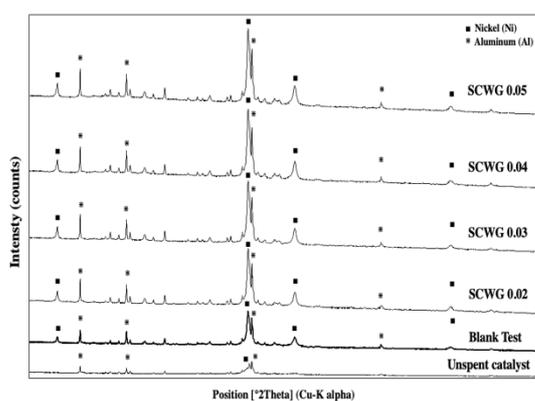


Figure 6. The XRD results obtained for all experiments conducted at 400 °C, 25 MPa.

Catalyst oxidation was also thought to cause the decline in catalyst efficiency. However, results from qualitative analysis using XRD presented in Figure 6 did not give the appearance of oxidation peaks. This rules out the speculation that the decline in catalyst efficiency was caused by its metal oxidation.

3.2 Characterization of Nickel catalyst after SCWG of vegetable oil

The unspent catalyst was characterized using gas sorption techniques and it was found out to have a surface area of 58.2 m²/g. However, after the gasification experiments conducted for 300 minutes, this surface area value decreased by 4 – 6 times. This suggests the loss of active surface area which may have caused the catalyst's decline in activity.

Table 1. Summary of catalyst characterization.

Catalyst	BET Surface Area (m ² /g)	Pore Diameter (Å)	Pore Length (Å)
Unspent	58.23	48.6	8.10
Blank	40.30	117	19.5
SCWG 0.02	13.09	172	28.6
SCWG 0.03	15.91	181.4	30.2
SCWG 0.04	9.14	176.9	29.5
SCWG 0.05	15.01	127.3	21.22

A blank test was conducted for 30 min to determine the morphology and change in particle characteristics of nickel catalyst if it is streamed in SCW only. As presented in Table 1, the surface area of the catalyst decreased to 40.3 m²/g. Also, the average pore diameter and length increased. This indicates that streaming the catalyst in SCW already gave a significant impact to its surface properties. Also, the drastic decrease of catalyst surface area after reacting it with the biomass suggests that the gasification reaction may have induced a harsh condition upon the catalyst. Since the decrease in surface area is almost the same in the four experiments, this indicates that the catalytic efficiency loss is not dependent on the biomass concentration. It could be that the molecules produced during the reaction may have been deposited on the catalytic pores at the initial phase of each experiment. These molecules cover the active catalytic area hindering its ability to gasify the biomass. Therefore, the higher the oil concentration, the more biomass goes unconverted as the reaction progressed. This could explain why the system fed with lower oil concentration had better performance as compared with the system fed with higher oil concentration.

To further elucidate its deactivation behavior, two experiments were added at varying total gasification time. Since the decline in catalytic performance was best observed at lower

biomass concentration, SCWG 0.02 experiment was repeated at 60 and 180 min.

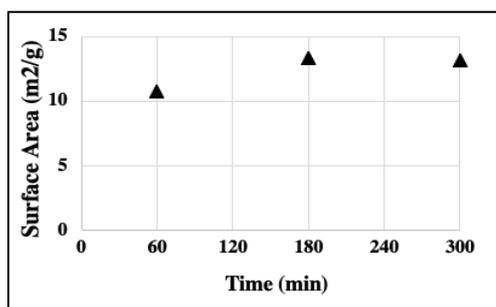


Figure 7. BET surface area variation of the catalysts obtained after the SCWG 0.02 experiments.

From Figure 7, the catalysts subjected to SCWG of oil at 2% for 60, 180 and 300 min have surface areas of 10.73, 13.31, and 13.09 m²/g, respectively. This decrease in surface area is speculated to be caused by species deposition produced from the reaction, particularly the carbon. SEM-EDX analysis was carried out to probe the catalytic surface.

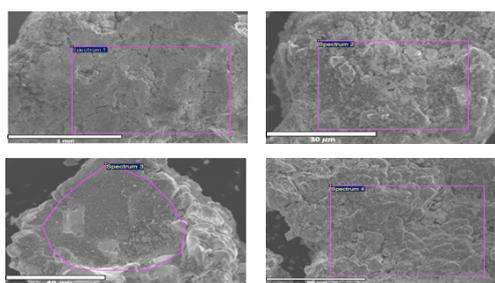


Figure 8. SEM image of the catalyst used during SCWG 0.02 at 60 min experiment.

From the manufacturer's data, the bulk of the unspent catalyst is mainly composed of 67.2% Ni, 31.9% Al, and 0.9% Mo. This also agrees with the EDX results obtained during preliminary studies. However, in Figure 8, after the 60 min reaction, the average weight fraction of the elements on the catalyst surface was 12.87% C, 46.71% Al, 37.26% Ni and 3.16% Mo. From the SEM images, the change in the catalytic surface is evident by the cracks and its rough surface. At first, the catalyst has a smooth surface (analyzed by SEM during preliminary data gathering) which was mainly composed of Ni; then as the particle was streamed in SCW, the surface slowly disintegrated and formed rough surface layers. For the catalyst particles subjected to SCWG for 180 mins, rough surface and cracks could be observed especially for Spectrum 1 and 4. The

References:

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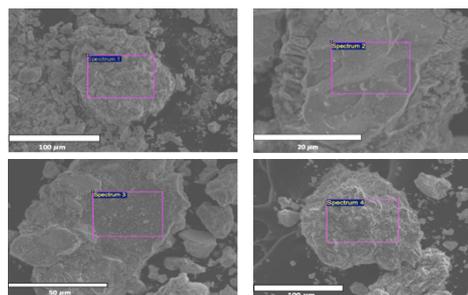


Figure 9. SEM image of the catalyst used during SCWG 0.02 at 180 min experiment.

average value of the elements detected from these spectrums are 34.99% C, 27.05% Al, 17.23% Ni and 20.75% Mo. However, for Spectrum 2 and 3, smooth, exposed surface can be seen. Moreover, the average values of the elements are 6.62% C, 13.56% Al, 76.09% Ni, and 3.75% Mo. In rough areas, the amount of Ni is less whereas C and Al mainly comprised the elemental distribution. Particle elution to the liquid phase was also considered and Ni and Mo in the order of ppb were detected in the effluent using ICP-MS analysis. The presence of higher Ni quantity at the start of the reaction and its gradual loss after exposure in SWCG of oil indicates the loss of active catalytic sites. However, the role of carbon in this mechanism should not be neglected. It could be that at the early onset of gasification, carbon from the biomass adheres on the catalytic surface. However, as deactivation moves to its advance stages, the outer catalytic surface is being eluted in the liquid phase which includes the Ni and C particles. From this, carbon deposition and sintering of the catalyst could be the possible causes of its catalytic activity decline.

4. Conclusion

The SCWG of vegetable oil using nickel catalyst was investigated using four biomass concentrations. It was found out that at lower biomass concentration, higher gas yields and efficiencies can be attained. However, as reaction progressed, the decline of catalytic performance was observed. Further observation of the nickel catalyst behavior in SCWG of oil led as with the assumption that this decline in catalytic activity may have been caused by carbon deposition and surface sintering.

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