

## Supercritical Water Gasification of Simulated Gutter Oil

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### Introduction

Used cooking oil is mainly generated in restaurants and domestic areas. In the management of waste cooking oil, most developed countries have a strict tracking system, which is formed from the collection, transportation and processing of waste edible fats and oils. This system helps to regulate the whole process and educate the nationals to form the awareness of collecting waste oil and develop good habits. However, it is unfortunate that until today, there are no collection facilities for used cooking oil in many countries, such as India and China. In the absence of collection facilities, used cooking oil from restaurants and domestic areas is discharged directly into the drainage system. In the drains, the oily part floats on top of the foul-smelling water phase. This oily phase is separated out by smugglers in mainland China. The waste oily material is then reprocessed, which is also known as gutter oil <sup>[1]</sup>. Gutter oil (GO) is a general term for waste cooking oil. It refers to the oil extracted from waste food or residue. With the rising price of crude oil on the international market and the resulting concerns about energy security, developing countries need to explore alternative and cheap energy sources to meet the growing energy demand. Along with people's living activities, a large amount of GO is generated, which can be considered as a sustainable renewable resource from the perspective of sustainable development. Therefore, it is recommended to utilize GO in biomass.

Supercritical water gasification (SCWG) is a hydrothermal process involving the reaction of biomass in hot compressed water above its critical point (374.1 °C, 22.1 MPa) to produce hydrogen enriched syngas from biomass and other organic wastes <sup>[2]</sup>. Meanwhile, with the hydrolysis of residual fat, oils, and grease from grease traps, diesel-like hydrocarbon fuel <sup>[3][4]</sup> is supposed to be produced. Therefore, the recyclability of GO in SCWG to produce hydrogen and diesel-like hydrocarbon is considered a sustainable way to minimize waste dumping while meeting the growing energy needs. Therefore, the main objective of this study is to investigate the decomposition of simulated gutter oil in supercritical water gasification. Specifically, it aims to identify the primary products (such as hydrogen and diesel-like hydrocarbons) produced in supercritical water conditions, investigate the effects of reaction parameters such as temperature and residence time on the product yield and distribution, and study the effect of catalyst addition.

### Experiment methods

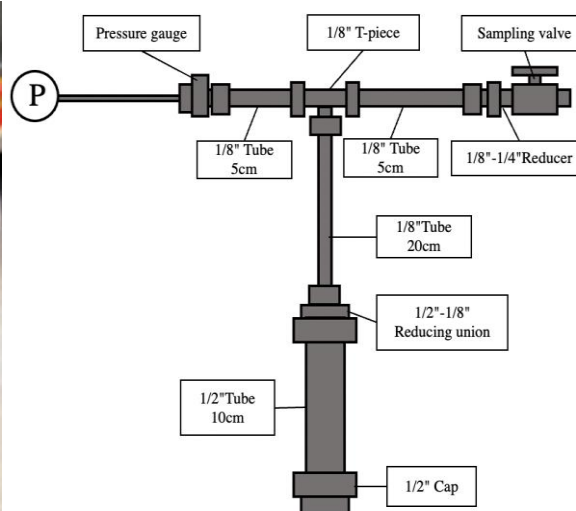
To keep the consistency of feedstock, it is necessary to prepare simulated gutter oil (SGO), instead of obtaining directly from the restaurant. Three common cooking oils were selected for this experiment, namely lard, soybean oil, and peanut oil. Based on the characteristics of different cooking oils and typical local ingredients, three cooking methods were chosen. The first is deep-fried chicken wings cooked in lard. Second, sliced lotus roots stir-fried in soybean oil. Last, Mapo tofu cooked in peanut oil. After cooking, the remaining dishes were then combined in a bucket, and after several weeks of acidity and denaturation, SGO with a poor grade was created, as shown in Figure1.

In this study the batch type reactor was used, as shown in Figure 2, that made of stainless steel

(SUS 316) with inner volume of 7.3ml was used in this experiment. The reaction part is a 10-cm tube with diameter of 1/2 inch and thickness of 1.65mm. In one side of the tube, a 1/2-inch cap is attached. In the other side, a 1/2-inch to 1/8-inch reducing union is connected with a 1/2-inch to 1/8-inch reducer. Then, it is connected to a 1/8-inch T-piece with a 20-cm 1/8-inch tube. The left two sides of the T-piece are connected to a pressure transducer and a sampling valve, which is used for collecting gas sample after hydrothermal reaction.



**Figure 1** Simulated gutter oil



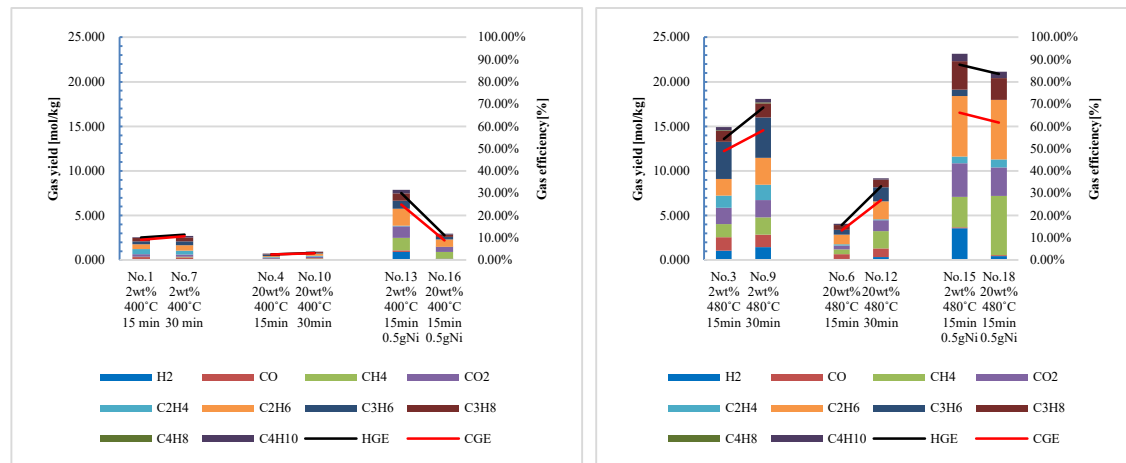
**Figure 2** Batch reactor

## Results and discussion

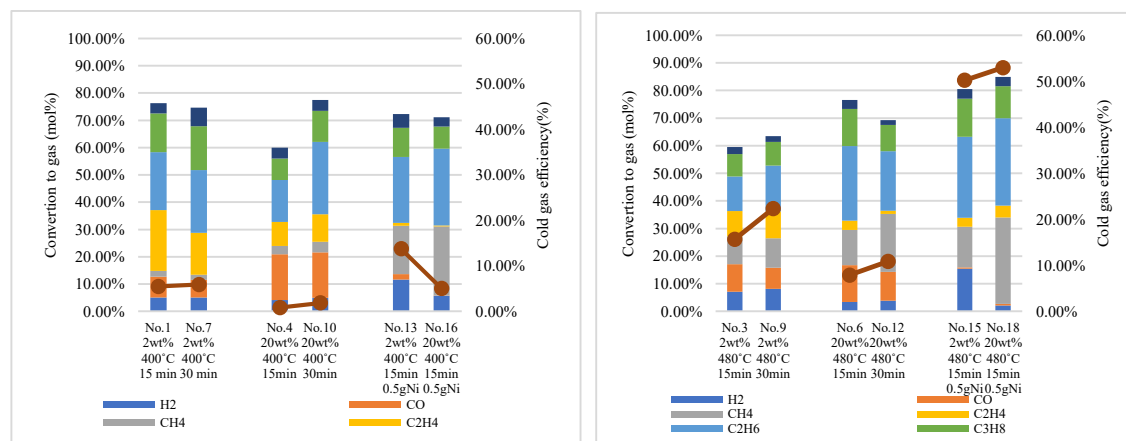
After SCWG of SGO, gas products were performed analysis with GC-TCD and FID. The Figure 3 shows the gas yield, carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HGE) of gas products. Among the non-catalytic experiments, the gas yield and gas efficiencies increase with increasing reaction temperature and decreases with increasing oil concentration. This indicates that the system is able to gasify biomass well at high temperature (480°C) but at low biomass (2 oil wt %) concentration conditions. It is worth noting that at low SGO concentration, the difference in gas yield and efficiencies improvement is not significant, however, at high concentration conditions, the increase in gas yield and efficiency was significant as temperature increasing. This implies that temperature is the key influencing factor for SGO gasification at high concentrations. In addition, the system was able to gasify biomass well within 30 min residence time.

The catalytic SCWG exhibited the same regular variation as the non-catalytic SCWG, where an increase in temperature and residence time resulted in an increase in gas product, but the opposite was true for an increase in SGO concentration. Looking at No.16, No.17 and No.18, C<sub>2</sub>-C<sub>4</sub> gas products make up a large portion of the gas product distribution. This indicates that larger hydrocarbons cannot be converted to the desired product by the system, but the opposite effect is observed in the low concentration SCWG process, where C<sub>2</sub>-C<sub>4</sub> hydrocarbons make up less than half of the overall product gas, as shown in No.13, No.14 and No.15. Moreover, the performance of the catalytic experiments was much better compared to the non-catalytic SCWG. First, the share of C<sub>2</sub>-C<sub>4</sub> gas products in the gas product distribution decreases with the addition of catalyst. This indicates that the system converts larger alkanes into the desired product with the help of catalyst. Secondly, the increase in CH<sub>4</sub> gas content implies that the steam reforming reaction is fully executed.

Comparing the results of these experiments, it can be concluded that the use of catalyst in the SCWG process leads to an improvement in the performance parameters.



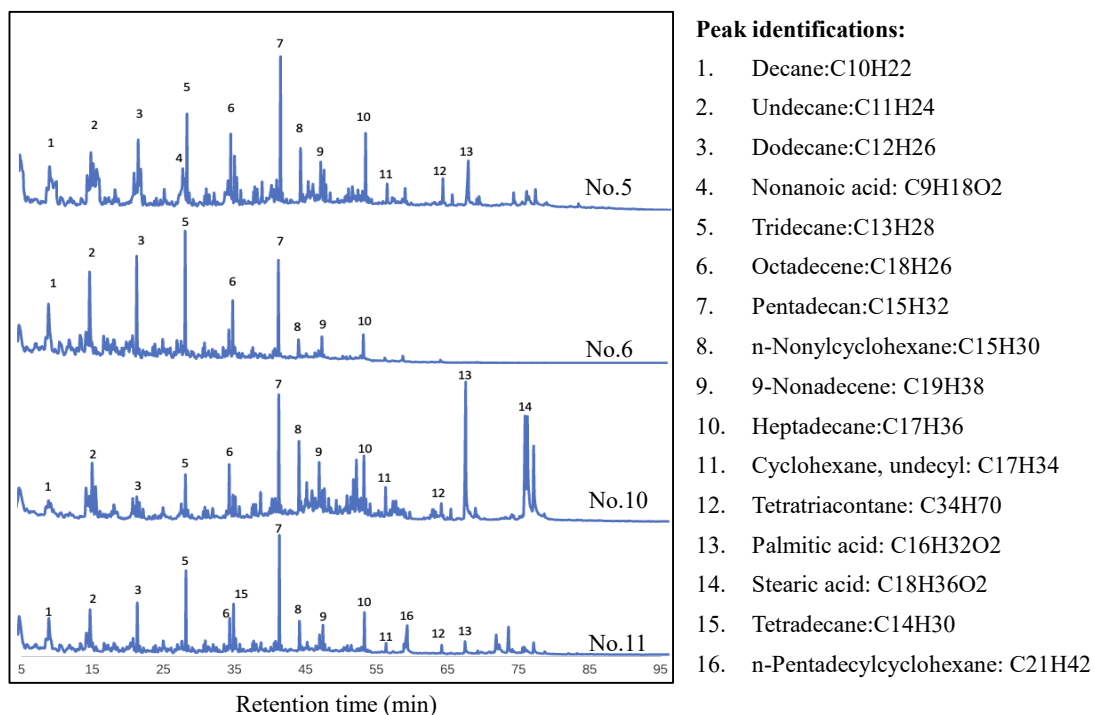
**Figure 3** Gas yield and gas efficiencies of SCWG at 400°C (left), 480°C (right)



**Figure 4** Cold gas efficiency of SCWG at 400°C (left), 480°C (right)

Figure 4 shows the cold gas efficiency (CoGE) of gas products. As time shifts from 15 to 30 minutes, CoGE increases with increasing residence time, however, conversely, CoGE decreases as the concentration of SGO changes from 2wt% to 20wt%, but this observation only occurs at low temperature. When the temperature reaches 480°C, CoGE increases with increasing biomass concentration. It can be assumed that the factor affecting CoGE is not the overall percentage content of the gas product, but the individual gas composition and gas yield ( $m^3/kg$ ). In addition, with the addition of catalysts, the content of hydrogen component, methane and ethane component increased, meanwhile, CoGE is large than non-catalytic experiments. It clear that the carbon monoxide content decreases and the amount of methane more than doubles. From these gas changes, it can be assumed that the CO and CO<sub>2</sub> methanation reactions are well achieved during the gasification process, but unfortunately the hydrogen content decreases by as much as half. The addition of catalyst in 2 wt% SGO leads to an increase in hydrogen production, while no significant improvement is obtained in 20 wt% SGO, but it promotes carbon gasification efficiency. Thus, it was shown that the high concentration of biomass feedstock was successfully gasified at high reaction temperatures. The performance of low concentration is better compared to high concentration of SCWG.

Figure 5 shows that the analysis of liquid samples by GC-MS, including No.5(450°C, 20wt%, 15min), No.6(480°C, 20wt%, 15min), No.10(400°C, 20wt%, 30min) No.11(450°C, 20wt%, 30min).



**Figure 4** GC-MS for liquid samples and peak identifications

GC-MS analysis of SGO confirms the presence of functional groups characteristic of hydrocarbons (alkenes, alkanes, ring-containing alkenes, and ring-containing alkanes, cycloalkenes, cycloalkanes, and aromatics). The hydrocarbons identified in SGO by GC-MS present carbon chain length ranging from C<sub>9</sub> to C<sub>34</sub>, indicating the presence of heavy gasoline compounds (C<sub>5</sub>-C<sub>10</sub>), kerosene-like fraction (C<sub>11</sub>-C<sub>12</sub>), light diesel-like fraction (C<sub>13</sub>-C<sub>17</sub>), and heavy diesel-like fraction (C<sub>18</sub>-C<sub>25</sub>), as defined in the literature [5]. The appearance of these functional groups proves the presence of diesel-like hydrocarbon in the liquid products after SCWG, which is valuable for further research.

## Conclusion

In this study, the decomposition of SGO in SCWG was investigated. It was found that supercritical water gasification proved to be a viable process for converting oil to desired gaseous products (H<sub>2</sub>) and diesel-like hydrocarbon under optimal conditions in laboratory-scale catalytic experiments. It can also be concluded that the system performs better at lower biomass concentrations than at higher biomass concentrations.

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