Catalytic cracking process of waste cooking oils using iron (Fe) catalysts to produce biofuel

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Abstract. Generally, there are 2 (two) methods of converting waste cooking oils into biofuel, namely by esterification of triglycerides into methyl esters (biodiesel), and utilizing thermal cracking of catalysts and hydrogenation to produce green diesel. The presence of oxygen content in waste cooking oils-free fatty acids will cause the formation of CO or CO₂ gas during the cracking process, so it is necessary to inject hydrogen to prevent it. In this study, an analysis of operating conditions, the characteristics of the biofuel produced, and the effect of the use of iron (Fe) catalysts were studied to convert used-cooking oil to biofuel. The hydrogenation of waste cooking oil is carried out at pressures of 30 and 40 psia, with heating temperature conditions of 250-350°C and operational pressures of 800-1000 psia. The maximum yield obtained was 31.7% (v) at 350°C and the use of 0.1% wt Fe catalyst. The resulting biofuel had a density of 0.8314 gr/ml and calorific value of 10152.66 cal/gr. By analysis contain of biofuel had C₁₀-C₁₅ 5.5%(v), C₁₅-C₁₈ 40.27%(v), C₁₈-C₂₀ 38.78%(v), and > C₂₀ 15.45%(v), respectively.

1. Introduction

A global environment that demands a better level of environmental quality encourages various energy experts to develop the energy that is more environmentally friendly and supports the security of sustainable supply. One solution to overcome this problem is by replacing petroleum with green diesel obtained from waste cooking oil with hydprocessing processes which can be alternative energy.

Cooking oil is one of the basic human needs as a processing tool for frying. The waste of cooking oil in Indonesia reaches more than 6.43 million tons per year [1] so that the right technology is needed to handle this waste by converting waste cooking oil to green diesel.

There are generally two ways to produce diesel from waste cooking oil, namely utilizing esterification which converts triglycerides to methyl-esters with the help of methanol and using of thermal treatment which includes thermal cracking, catalysts, and hydrotreating. The hydrotreating is considered as the most efficient method in waste cooking oil cracking. This is because the hydrogenation process consumes less heat energy and minimizes coke formation due to the presence of hydrogen [2]. It involves the hydrogenation of the double bonds of the chain and removes Oxygen with metal as the catalyst. The hydrotreating of waste cooking oil leads to C₁₅-C₁₈ hydrocarbons production as green diesel [3].
2. Experimental

2.1. Material
Waste cooking oil was obtained from some small restaurants and used without any purification. Waste cooking oil was used 2 L for 1 run. Iron Fe was purchased from Sigma-Aldrich Chemical Company (St. Louis, MO, USA) as a catalyst.

2.2. Functional Design approach
The Catalytic Hydrogenation method several components that have their respective roles, namely:

1. Green Diesel Reactor; Serves to convert used-cooking oil and hydrogen through a hydraulic process into green diesel. This reactor is made of stainless steel with a height of 40 cm, an outer diameter of 2.5 inches and a thickness of 10 mm.
2. Heater; Serves as a source of heat for the reaction needs of the reactor. This heater type belt heater with a height of 30 cm and a diameter of 2.5 inches. This heater has a capacity of 1000 Watt-hour 220 Volt.
3. Cooler; Serves to change the phase of green diesel products from gas to liquid. This cooler is divided into two parts: shell and tube. The cooling fluid in the shell is water while the cooled product flows in the tube

2.3. Characterization
The elemental composition of green diesel was determined using an analyzer GC-MS (Agilent Technologies 7890A gas chromatograph 5975C mass selective detector). The density of green diesel was determined by ASTM D4052 and for heating value used by ASTM D240-02

3. Results and Discussion
The long chain of hydrocarbons crack to short-chain have three methods. The thermal cracking with high temperature for the lighter product as the first method. The second method uses catalytic cracking. The last method is catalytic hydrocracking and occurs in the presence of a bifunctional catalyst and a high hydrogen pressure. The catalytic hydrocracking process consumes less thermal energy and the presence of hydrogen minimizes coke formation for liquid product [4].

In this study, the authors have conducted various operating conditions to find the optimum conditions from the hydrogenation of waste cooking oil to green diesel. One of the parameters reviewed by the author is the volume of green diesel. In this research, the product consisted of two phases, gas and liquid. The gas phase is believed to be propane, water, carbon dioxide, and hydrogen that does not react. The influence of operating conditions on green diesel production can be seen in Figures 1.

![Figure 1. Temperature and H₂ pressure on product of green diesel](image_url)
Based on Figure 1 to get the highest volume of green diesel is influenced by the higher hydrogen pressure operational and reaction temperature. High temperatures favored making waste cooking oil to liquid hydrocarbons consisting mainly of gasoline. That initial hydrogen pressure in a reactor made for the catalytic cracking step, and hydrogenation and hydrocracking were possible for the cracking and rearrangement to yield light hydrocarbon molecule [5].

![Figure 2](image-url)  
**Figure 2.** Temperature and catalyst relation to operating pressure

Figure 2 also proves the effective function of the catalyst to accelerate the reaction due to a large amount of gas in the reactor.

In addition to getting the relationship between product temperature and volume, the authors also get the effect of temperature on the density of the product. To determine the effect of operating conditions on product density in Figure 3.

![Figure 3](image-url)  
**Figure 3.** The density of green diesel

The results are known from Figure 3 that the lowest product density is in the operating conditions where hydrogen supply and high reaction temperatures occur. This is because in these operating conditions hydrogenation works best. The hydrogenation process is best because the low density
proves that the chemical chain is more straight than the others, which means that hydrogenation has structure C15-C18.

That hydrogenation works better at higher temperatures; the results of GC-MS analysis have also proven it. In GC-MS analysis, the samples taken are samples in operating conditions where the hydrogen pressure enters 30 psi and the reaction temperature is 300°C and 350°C. It can be seen in Table 1.

| Component (%) | Temperature (°C) |
|---------------|-----------------|
|               | 300             | 350             |
| C10-C15       | 10,47           | 5,5             |
| C15-C18       | 5,64            | 40,27           |
| C18-C20       | 38,5            | 38,78           |
| >C20          | 45,42           | 15,45           |

Products at low temperature operating conditions have a hydrocarbon composition with atomic number C more than 20. Green diesel products at high temperature operating conditions have C15-C18. Results with the Fe catalyst process indicated that chains of C15-C18 were 40.27% that established with thermal cracking in 350°C. C15-C18 chains produced by the hydro-deoxygenation (HDO) reaction. The Fe/NZ catalyst process in producing C16 or C18 chains produced by the HDO reaction [6]. The addition of metals promises to be useful catalysts, as they can act as Lewis acid sites on yields products. To indicate the presence of new Lewis acid sites on the Fe sites of Fe/Beta catalysts [7]. Fe direct to HDO direct C–O bond cleavage [8].

The following reaction mechanism that occurs in the hydrogenation process of waste cooking oil into green diesel can be seen in Figure 4.

![Figure 4. Reactions in the hydrotreatment of generic vegetable oils and fatty acids [9]](image)

One of the chemical properties that determine the quality of fuel is the amount of energy contained in the fuel. This value is usually termed the heating value. So the authors analyze the heating value of green diesel products. The heating value was used by the Bomb Calorimeter (ASTM D240-02). The test results can be seen in Table 2 also compare with previous research.
Table 2. Summary on studies of different hydrodeoxygenation reaction systems

| Sample          | Reactor Type | React Cond H2 | Catalyst | Main Product | Perform. | Density (g/ml) | Heating value (cal/gr) | Ref |
|-----------------|--------------|---------------|----------|--------------|----------|----------------|------------------------|-----|
| Waste Cooking   | Batch        | T = 350°C     | Fe = 0.1 gr | C15-C18=40.27 | Yield   | 0.8314 | 10152.67 | This work |
| Oil A           |              | P = 40 psi    |          | C18-C20=38.78 |         |          |            |                  |
| Waste Cooking   | Batch        | T = 300°C     | Fe = 0.1 gr | C15-C18=40.27 | Yield   | 0.8454 | 10121.76 | This work |
| Oil B           |              | P = 30 psi    |          | C18-C20=38.78 |         |          |            |                  |
| Vegetable oil   | E cofining   | 1.5-3.8       |          |              |         | 88-89%v | 0.78   | 10516.3 [10] |
| Waste Cooking   | Fixed batch  | T = 350°C     | Ru = Al13 | C15-C18 n-paraffins | Yield:82.1 | 0.78 | - | [2] |
| Oil             |              | P = 2 MPa     | monmorillo | |         |          |            |                  |
|                 |              | H2/oil ratio  = | nite      | |          |            |            |                  |
| Palm Oil        | Batch        | T = 375°C     | Nat. Zeolit =3% | C15=33.04% | Yield:58 | - | - | [6] |
|                 |              | P = 12Bar     | | |         |          |            |                  |
|                 |              | H2 = 2 h      | Fe/Nat. | C15=59.19% | Yield:89 | - | - |                  |
|                 |              |               | Zeolit =3% | | |          |            |                  |

Thermal cracking with hydroprocessing used Fe metal catalysts from waste cooking oil to diesel range hydrocarbon C15-C18. However, Green diesel is produced yield 31.70% and still goes further to get efficiency to compare the other research. Waste cooking oil with a ruthenium catalyst supported on Al-polyoxocation-pillared montmorillonite used bio-hydrogenated diesel by hydrotreatment. The process was simultaneously deoxygenated on hydrocarbon products (98.9 wt %) were n-C18H36, n-C16H34, and n-C15H32.[2].

The obtained materials were tested for the conversion of palm oil into diesel-range hydrocarbons (C15-C18) under conditions of 375°C and 12 bar H2 for 2 h. NZ and Fe/NZ produced a liquid hydrocarbon with straight-chain (C15-C18) alkanes as the most abundant products. The liquid yield product exhibited a higher conversion into diesel-like hydrocarbons, reaching more than 58% and 89% when the natural zeolite (NZ) and Fe/NZ metal loading (3 wt.%) catalysts, respectively [6].

4. Conclusions
Based on the results of research on the production of green diesel from waste cooking oil with catalytic hydrogenation method. The product volume obtained it is concluded that the higher the operating temperature (350°C), the volume of green diesel products coming out is increasing. H2 pressure is also very influential because of the higher the pressure, the higher the operating temperature produced.

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