Abstract
This study aims to compare the amount of carbon footprint (CF) in a laboratory-scale production of upgraded biodiesel from used vegetable oil (UVO) by different energy sources. The system boundary marked by a Business to Business (B2B) approach is applied in two scenarios and includes pre-treatment, biodiesel conversion and quality improvement via thermal cracking and catalytic cracking reaction using Zeolite HZSM-5 as a catalyst. The first scenario is carried out by using electricity as a heating energy source in thermal cracking reaction while the second scenario is carried out by using LPG gas as a substitute for electricity. The primary data were directly collected from production and the secondary data were obtained from existing databases relevant to this study’s topic. The result of the study shows that using LPG gas as a substitute for electricity evidently reduces the total amount of CF by approximately 31%. However, the major cause of GHG emission in the two scenarios is electricity consumption.

Keywords: Upgraded biodiesel, carbon footprint, business to business analysis, used vegetable oil

1. Introduction
Erratic weather events such as extreme temperatures and unusual approaches of violent winds are currently taking place in many areas of the world. These phenomena can be considered as the impacts of carbon dioxide and GHG emissions in the earth’s atmosphere. The fact that GHGs absorb, preserve and accumulate the earth’s radiating heat eventually leads to global warming and climate change. One of the main causes of carbon dioxide emission is fuel combustion from transportation in which fuel is more and more necessary nowadays. Alternative energy or renewable energy including biodiesel from used vegetable oil is thus introduced as an energy source which will help reduce GHG emissions and air pollution resulting from sulfur dioxide (SO₂), Hydrocarbon, soot and garbage [1,2]. The act of sending used materials back to the production chain or reusing them can pave the way for a circular economy that not only solves garbage problems but also promotes social, economic and environmental sustainability [3].

However, biodiesel from UVO still has limitation and is less effective than diesel fuel when it is practically used with engines. As UVO biodiesel has high viscosity and low calorific value, this results in a high fuel consumption rate. In addition, its high level of oxygen accelerates oil deteriorate and, in the long run, can bring about damages in engine parts due to sludge formation. From the aforementioned defects, there are many research projects that seek to develop the production of high-quality biodiesel [4-8]. One of them is the project called cracking process development for generating high grade bio oil [9] which develops the production of upgraded biodiesel from transestered biodiesel from used vegetable oil through Thermal cracking under nitrogen atmosphere and Catalytic cracking by using HZSM-5 as a catalyst. This study reveals that the upgraded biodiesel has lower viscosity and higher calorific value that are close to the quality of the commercial diesel as seen in Table 1. After that, it evaluates a prime cost of
upgraded biodiesel in a laboratory-scale production and shows that biodiesel’s cost is higher than that of diesel fuel because enormous amounts of electricity are consumed to heat biodiesel up to 500°C and enable thermal cracking. Instead of electricity, this study tries using LPG as another heating energy source and discovers that the cost of biodiesel production is reduced around 83%. But before choosing any energy source, there should be concerns not only of quality and economic suitability but of environmental issues in order to be used as a criterion for producing fuel in the same quantity with the least environmental impact. Therefore, this study aims to compare the amounts of GHG emission in the upgraded biodiesel production by using different energy sources.

Table 1. The calorific value and viscosity of oil.

| Parameter                  | Unit  | UVO   | Biodiesel | Upgraded Biodiesel | Commercial Diesel |
|----------------------------|-------|-------|-----------|--------------------|-------------------|
| Calorific value            | MJ/kg | 38.80 | 38.93     | 43.51              | 46.70             |
| Viscosity (at 40 °C)       | cSt   | 4.55  | 5.92      | 4.52               | 3.73              |

2. Methodologies

2.1. Study goal and scope definition

**Goal and Functional Unit**

This study aims to compare the amounts of CF in the production of upgraded biodiesel from used vegetable oil (UVO) by using different energy sources in a laboratory-scale production. Functional unit (FU) employed in this study is one liter of upgraded biodiesel derived from UVO.

**Scenario Setting and System Boundary**

This study will estimate GHG emission in the upgraded biodiesel production in two scenarios as Table 2. The processes which are employed in both scenarios include pre-treatment and biodiesel conversion that are processed through transesterification reaction, and quality improvement that is processed through Thermal cracking and Catalytic cracking reaction. The first scenario is carried out by using electricity as an energy source to heat the reactor up to 500 °C and enable thermal cracking while the second scenario is carried out by using LPG gas as a substitute for electricity.

Table 2. The two scenarios of upgraded biodiesel production description.

| Scenarios                  | Description                                                                                           |
|----------------------------|-------------------------------------------------------------------------------------------------------|
| Scenario 1                 | Upgraded Biodiesel production includes pre-treatment biodiesel conversion and quality improvement stage that use electricity as an energy source to heat the reactor up to 500 °C and enable thermal cracking. |
| (Conventional)             |                                                                                                       |
| Scenario 2                 | Upgraded Biodiesel production includes pre-treatment biodiesel conversion and quality improvement stage which using LPG gas as an energy source to heat the reactor up to 500 °C and enable thermal cracking. |

The system boundary of the carbon footprint evaluation in the production of upgraded UVO biodiesel, as shown in Fig. 1 and 2, is delineated by a Business to Business (B2B) approach in which CF is defined as kg CO₂ eq FU¹.
2.2. Inventory analysis, data sources and main assumptions

Both primary and secondary data were used for the analysis of this study. The primary data such as raw materials, energy sources, chemicals, by-products, co-products and others were directly collected from laboratory production. Calculations and assumptions were drawn from the secondary data that were obtained from existing databases such as Ecoinvent data v3.0 available in SimaPro V.9, and relevant Thai and international journals.

Titration with Sodium Hydroxide (NaOH) was applied to test the percentage of free fatty acid (%FFA).
of used oil at the pre-treatment stage since the used oil with high %FFA, which will be transformed into biodiesel, might cause undesirable side reactions such as saponification problems and catalysis losses [9]. From the %FFA test, while the UVO’s %FFA of more than 1% would be reduced to be less than 1% by esterification reaction [11], the UVO’s %FFA of less than 1% could indeed proceed to biodiesel conversion stage without pre-treatment. At biodiesel conversion stage, NaOH catalyst mixed with Methanol (CH$_3$OH) solution at 60 ºC was used in transesterification reaction. This stage might have glycerin as a by-product which would be subsequently used to make refuse-derive fuel (RDF). After that, transesterification reaction, condensation and purification were processed through fractional distillation. At the final stage, the quality of UVO biodiesel was improved via thermal cracking under the temperature of 500 ºC with Nitrogen gas flow and catalytic cracking in fixed bed reactor. HZSM-5 was used as a catalyst in this study. Then the upgraded biodiesel was purified by fractional distillation.

2.3. Carbon footprint calculations

According to Thailand Greenhouse Gas Management Organization (TGO), ‘Verification sheet’ [12] were used to calculate carbon footprint. The collected data were calculated in terms of mass balance, energy balance, chemical balance and allocation per FU. The reason why mass allocation was calculated in this study is that several products came from fractional distillations. The amount of CF was evaluated afterwards in accordance with the Life Cycle Assessment (LCA) methodology following the International Organization for Standardization (ISO) standards ISO 14040 (ISO, 2006a) [13] and carbon footprint of product (CFP) concept.

The total GHG emission in the production of upgraded biodiesel was calculated by multiplying activity data and emission factor of each activities as equation 1. The amount CF was presented in CO$_2$ equivalent (CO$_2$ eq.), so a measurement of all GHGs was converted into kg of CO$_2$ eq. with reference to the global warming potentials for 100-year time horizon.

$$CFP = \sum (A_i \times EF_i)$$

(1)

where $CFP$ denotes the carbon footprint of product (kg CO$_2$ eq./FU), $A_i$ is activity data of activity i (kg, liter, kWh or etc.), and $EF_i$ is emission factor of activity i (kg of CO$_2$ eq per kg, liter, kWh or etc.).

3. Result and Discussion

The three-time %FFA test of UVO shows the amounts of 0.794%, 0.768% and 0.717% which are not over 1%. Therefore, it is unnecessary to treat UVO prior to the biodiesel conversion stage processed through transesterification.

In Table 3, the carbon footprint (CF) of biodiesel from conversion and quality improvement stages is demonstrated in scenario 1 and 2. After summarizing CF in both stages, the total amount of CF of the upgraded biodiesel of scenario 1 was 4.172 kg CO$_2$ eq/ l of upgraded biodiesel consisting of 0.169 kg CO$_2$ eq/ l from the biodiesel conversion stage and 4.003 from the quality improvement stage. The major cause of GHG emission in biodiesel conversion stage is 59% emission from the acquisition of UVO while the succeeding causes are 19% emission from NaOH and CH$_3$OH mixing and 13% emission from electricity consumption. In quality improvement stage, electricity consumption is the major contributor to CF with 89% of GHG emission whereas the succeeding contributors are HZSM-5 catalyst and used Nitrogen gas with 10% and 0.5% of the emission, respectively.

In scenario 2, the total CF of the upgraded biodiesel gathered from both stages is 3.188 kg CO$_2$ eq/ l, consisting of 0.156 kg CO$_2$ eq/ l from the biodiesel conversion stage and 3.032 kg CO$_2$ eq/ l from the quality improvement stage. In the same fashion, this scenario shows that the major cause of GHG emission in biodiesel conversion stage is 60% emission from the acquisition of UVO while other succeeding causes are 18% emission from NaOH and CH$_3$OH mixing and 14% emission from electricity consumption.
consumption. In quality improvement stage, again, electricity consumption is the major contributor with 70% of GHG emission while other contributors are HZSM-5 catalyst and LPG gas combustion with 13% and 12.5% of the emission, respectively.

Table 3. Carbon footprint (CF) of biodiesel conversion and quality improvement.

| CF of biodiesel conversion and quality improvement | Scenario 1 (kg CO₂ eq/ l of upgraded biodiesel) | Scenario 2 (kg CO₂ eq/ l of upgraded biodiesel) |
|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| Used vegetable oil                               | 0.100                                            | 0.094                                            |
| NaOH and CH₃OH mixing                            | 0.033                                            | 0.029                                            |
| Rubber gloves                                    | 0.011                                            | 0.011                                            |
| Tap water                                        | 0.002                                            | 0.001                                            |
| Electricity                                      | 0.023                                            | 0.022                                            |
| **Biodiesel conversion**                         | **0.169**                                        | **0.156**                                        |
| Nitrogen gas                                     | 0.020                                            | 0.020                                            |
| HZSM-5                                           | 0.402                                            | 0.387                                            |
| Tap water                                        | 0.018                                            | 0.018                                            |
| Electricity                                      | 3.563                                            | 2.122                                            |
| LPG gas                                          | 0.000                                            | 0.102                                            |
| LPG gas (Combustion)                             | 0.000                                            | 0.382                                            |
| **Quality improvement**                          | **4.003**                                        | **3.032**                                        |
| **Biodiesel conversion and Quality improvement** | **4.172**                                        | **3.188**                                        |

The chart in Fig. 3 is a comparison of the top five contributors to GHG emissions in the upgraded biodiesel production. These contributors include acquisition of UVO, NaOH and CH₃OH mixing, electricity consumption (from both biodiesel conversion and quality improvement stages), HZSM-5 catalyst and LPG gas. It can be concluded that electricity consumption in quality improvement stage is the major contributor to CF as it occurred in many processes. In scenario 1, electricity has been consumed by the first reactor in order to heat UVO up to 500 ºC for thermal cracking reaction. In addition, it has been consumed by the second reactor in order to control the temperature, enable catalytic cracking reaction and operate the pump used to condense the oil vapor once reactions and fractional distillation completed. On the other hand, in scenario 2, electricity has been used to control the temperature for catalytic cracking reaction and to operate the pump. It is evident that the amount of CF from electricity consumption has been reduced. However, GHG emission still occurs mainly in the use of LPG for heating. The emission is also generated by the catalyst in catalytic cracking in quality improvement stage and acquisition of UVO in biodiesel conversion stage.

Fig. 3. The total CF of upgraded biodiesel from UVO production

It is suggested in this study that LPG gas which is used instead of electricity as a heating energy source is an extremely interesting alternative since, in the same amount for heating, the production cost of LPG is lower than that of electricity. Furthermore, LPG gas can reduce GHG emission in the quality improvement stage by 37%. It should be noted, however, that this CF evaluation of upgraded UVO
biodiesel was only conducted in a laboratory-scale production. Despite the high level of CF in comparison with the average CF of biodiesel in Thailand [14], it cannot be directly compared to the average CF which has been generally evaluated in many studies due to different objectives, assumptions and system boundaries. In addition, it is expected that, on a pilot or commercial scale, this upgraded biodiesel will possibly reduce CF in a more optimized operation and become a potential competitor in the biofuel market.

4. Summary

As the CF evaluation of upgraded biodiesel from UVO in this study has been carried out in a laboratory-scale production through a B2B boundary approach. The result reveals that there is a total of 4.172 kg CO$_2$ eq/ l of CF from the upgraded biodiesel in scenario 1. The major cause of GHG emission in this upgraded biodiesel production is electricity consumption while other causes are HZSM-5 catalyst and UVO acquisition. The total CF in scenario 2, on the other hand, is 3.188 kg CO$_2$ eq/ l of upgraded biodiesel. The main cause of GHG emission in the second scenario is electricity consumption while other causes are HZSM-5 catalyst and LPG combustion. Using LPG gas as a substitute for electricity and a heating energy source in the quality improvement stage is proved to reduce the amount of CF by 37% and the total amount of CF by approximately 31%. However, to optimize an operation that can effectively reduce CF of upgraded biodiesel in UVO production is quite a challenge.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Pichamon Intthiyot, Sate Sampattagul, Nivit Charoenchai were conceptualize the research. Pichamon Intthiyot were conducted to the research and undertook the experiment data collection. Sate Sampattagul, Nivit Charoenchai managed the project and reviewed the work. All authors had approved the final version.

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