# Evaluation of Biodiesel Production in a Hydrodynamic Cavitation Reactor from Waste Cooking Oil

Daniel J. Contreras, Luis A. Gomez, Dionisio Malagón-Romero*

Semillero Energía y Termofluidos, GEAMEC, Universidad Santo Tomás, carrera 9 n.° 51-11, Bogotá, Colombia
dionisiomalagon@usantotomas.edu.co

The production of biodiesel from waste cooking oil (WCO) has been studied by transesterification reaction in an agitated reactor. An alternative to decrease heating and reaction time is to use a hydrodynamic cavitation reactor. The objective of this work was to evaluate biodiesel production in a hydrodynamic cavitation reactor using WCO. A response surface methodology (RSM) was used to find the best experimental conditions. Yield and energy consumed per kilogram of biodiesel produced (ECPKB) surfaces were adjusted. The independent variables were: the methanol-oil molar ratio (6:1 - 5:1 - 4:1) and the percentage of potassium hydroxide catalyst (1% and 0.5%). The flow rate, temperature, electrical energy consumed, and reactor inlet and outlet pressures were monitored. According to the RSM, the optimum production parameters were: molar ratio (MR) 4:1 and 0.5% potassium hydroxide catalyst percentage (KOH). The biodiesel produced was analyzed by a gas chromatography, a cetane index and heat value laboratory tests according to ASTM D6751 standard. Due to high content of methyl esters (above 98%) for 5:1 MR and 0.5% KOH these conditions were selected as the best for production. These conditions led to the highest yield of 1.07 and 74.07 kJ/kg of ECPKB. The reaction time was less than 10 minutes for all conditions, indicating a breakthrough for biodiesel production.

## 1. Introduction

The energetic needs of the world depend mostly on the production and extraction of fossil fuels, natural gas and coal (Khan et al., 2017). Currently, the world is facing two challenges: reducing dependence on petroleum and controlling pollution rates (Rehan et al., 2018). Due to them, the duty arises to protect the environment and expand alternative fuel resources (Moazeni et al., 2019). The increasing demand for unconventional energetic resources has caused the implementation of biofuels, such as biodiesel, to gain popularity mainly because of its cleanliness and the fact that it can be produced from domestic and renewable resources (Suresh et al., 2018). Conventional biodiesel is a fuel obtained by transesterification, which is the conversion of triglycerides from animal fats and vegetable oils into fatty acid methyl esters (López et al., 2015), this method requires a heating and then a mixing stage of the fat or oil, methanol and catalyst, this whole process takes between two and three hours (López et al., 2015). Biodiesel has proven to be environmentally friendly as it produces 83% less greenhouse gases presenting itself as a great and viable alternative with similar characteristics to fossil fuels (Suresh et al., 2018). This is one of the main reasons why there is a need to explore non-conventional biodiesel production methods such as cavitation.

Cavitation is a phenomenon characterized by the formation of tiny vapor "bubbles" in the flow or on solid surfaces in contact with that flow (Ladino et al., 2016). The most common physical requirement for cavitation is that the absolute pressure of the fluid drops below the value of the vapor pressure at the current temperature (Sharma et al., 2008). This could be used to increase turbulence during a chemical reaction in a hydrodynamic equipment (Ladino et al., 2016). This induces cavitation with the aim of generating the intensification of a chemical reaction (Gogate, 2008). There are two configurations of hydrodynamic cavitation reactors, sonochemical and hydrodynamic cavitation; of these two categories, the hydrocavitation is the most common with orifice plate configuration (Gogate, 2008). One of the advantages of using hydrocavitation is the high yield (96%) with lower energy consumption and times of less than 15 min (Bokhari et al., 2016). The most common configuration

consists of a pump pushing flow through a nozzle-orifice plate configuration where cavitation takes place (Chuah et al., 2017)., whereby changes in the normal flow conditions generate high speeds and shear flows resulting in aggressive and fast instigation of cavitation (Gogate, 2008). The application of hydrodynamic technology decreases reaction time, and can be easily scaled up to meet the industrial demands compared to other cavitation methods (Wu et al., 2018).

The main objective of this paper is to evaluate biodiesel production in a hydrodynamic cavitation reactor from collected WCO. The reactor used is an orifice plate configuration, which was previously designed by the authors and the results could be scalable to industrial level.

## 2. Materials and Methods

### 2.1 Materials

For this study, 140 liters of WCO were collected from several fast food restaurants in Bogotá (Colombia). Methanol (99% purity, Panreac, Spain) was used as the alcohol for the reaction. Potassium hydroxide (85%, Panreac, Spain) was used as the alkaline catalyst. Phenolphthalein (99.5%, Bioquigen, Colombia), potassium iodide (99%, Panreac, Spain), starch from potato soluble (Panreac, Spain), chloroform (Chemi, Colombia), sodium thiofulsate (99.5%, Bioquigen, Colombia), Wijs´ reagent (Panreac, Spain) and Ethanol (99.5%, Panreac, Spain) were also implemented for WCO characterization.

### 2.2 Methods

### Filtration and characterization of WCO

To remove particles and impurities that could affect the experiment, the WCO was filtrated using a 3hw grade filter paper (Boeco, Germany) and subsequently stored in plastic containers at room temperature (13°C). Density (ASTM D-5), acidity index (ASTM D-1980), iodine index (ASTM D-5554), saponification index (ASTM D-5558) and peroxide number (ASTM D-1832) where determined according to the above standards. Viscosity was also reported at a temperature of 40 °C using a Cannon viscometer LV model 2020.
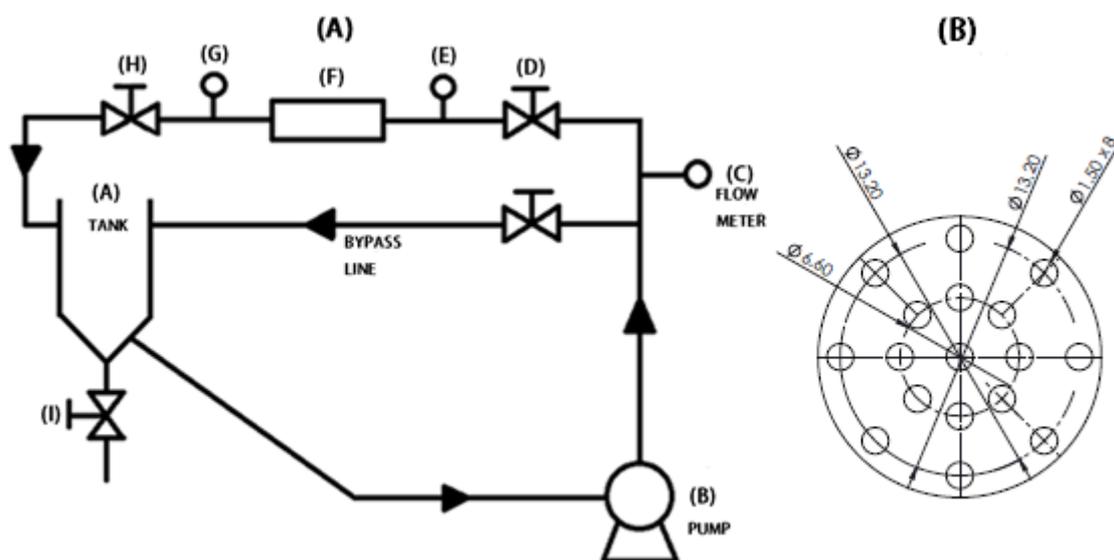
### Test and reaction system



Figure 1: (A) The configuration of the hydrodynamic cavitation reactor. (B) The configuration of the orifice-plate was used in the reactor.

Figure 1 shows the assembly of the reactor in which the production process was carried out. This reactor was designed by Universidad Santo Tomás (Bogotá, Colombia) and is composed of a 5-liter tank (A), an IHM JET1100G1 pump (B), a LFM SM6004 Thermocouple flow meter (C), two gate valves (D) and (H), two pressure gauges (E) and (G), a reactor (F) consisting of an orifice plate 17.15 mm in diameter connected to a nozzle and a diffuser and a needle valve (I). The whole reactor has a capacity of 8 liters and was constructed of 1-inch diameter pipes of SCH 40 INOX 304 steel. The mixture of WCO and methanol with the already diluted KOH was

poured into (A), (A) is sealed and (B) starts working. (B) Pushes the fluid through (C) which measures flow and temperature; then, the stream passes to (D) which together with (H) set the working pressure. Before and after the reactor pressure was measured by the means of (E) and (G). When the flow passes through (F) the transesterification produced by cavitation begins. Finally, the flowing substance returns to (A) and recirculates through the installation until the predefined time is reached. (I) has the purpose of emptying the machine as well as taking samples when required.

**Design of experiments**

The experiment was built around the objective of determining the optimal conditions for ECPKB and yield in biodiesel production using a hydrodynamic cavitation process. Yield is the ratio of methyl esters produced to the weight of the initial oil and conversion is the ratio of the weight of the converted oil to the weight of the initial oil (Alarcón et al., 2017). The variables were potassium hydroxide concentration (1% and 0.5%) and methanol to WCO molar ratio (6:1, 5:1 and 4:1). The difference between reactor inlet and outlet pressures was maintained at 2 bar. Each experiment was performed for 6 liters of WCO. Samples of 100 ml of the product were collected at time 0 and every 5 minutes for 30 minutes for subsequent separation with a decantation funnel. Three phases were obtained into decantation funnel: Glycerol phase (in the lower layer), biodiesel phase (middle layer) and oil phase (in the upper layer). The biodiesel phase was collected and washed three times with distilled water until a neutral pH was achieved. This process allowed the removal of glycerol, methanol and excess catalyst. Temperature, flow rate, pressure in gauge 1, pressure in gauge 2, voltage and electric current were monitored. The ECPKB was calculated from voltage, electric current and time used in each experiment. The RSM analysis was permormed for two output variables: ECPKB and Yield (biodiesel mass to oil mass ratio) (Alarcón et al., 2017). The Input variables were molar ratio and KOH concentration. The data was adjusted to a quadratic model with the free test of the Minitab software. This, with the aim of finding a surface that best fits the production process and shows the optimal production point in terms of MR and KOH%. The second order model adjusted was:

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1^2 + \beta_4 x_2^2 + \beta_5 x_1 x_2 \tag{1}$$

Where $\eta$ is the output variable, $x_1$ is the molar relation and $x_2$ is the catalyst concentration.

**Characterization of the biodiesel**

The heat of combustion was performed under the ASTM D240 standard and with the following materials: an IKA C 2000 Basic S1 calorimeter and a Mettler-Toledo AB 204 (Switzerland) analytical balance used in isoperbolic mode, extra dry industrial oxygen grade 2.7 at 30 bars. A Julabo F12 Thermostat at 25°C controlled the calorimeter jacket temperature. As instructed in ASTM D 240 sulfur content was determined with a Spectronic Genesys 5 spectrophometer (Thermo Scientific, Masachusetts, USA) to make the necessary corrections. Gas chromatography was performed with Agilent 6820 (Agilent technologies, China) equipped with a SGE 12m X 0.53mm X 0.15µm capillary column and a flame ionization detector (FID). After the 1µl is injected, the oven maintains a 120°C temperature for 1 minute and then heats up at a rate of 2.25°C/min until a temperature of 380°C is reached. The temperature of injection port and detector temperature was 259°C. Nitrogen with a flow rate of 6 ml/s was used as the drag gas. The corresponding Cerity QA/QC (Agilent technologies, Germany) software acquired and processed all the data. Finally, cetane index was performed according to ASTM D4737 using the following equipment: Precision PS Scientific Series 10Z9 (Chicago, USA), a CASIO (China) chronometer and a Silver Brand (USA) thermometer.

## 3. Results and discussion

### 3.1 Oil characterization

The results for oil characterization are shown in Table 1. The density, saponification value and viscosity obtained by WCO are close to those reported in previous WCO characterizations (Maddikeri et al., 2014). However, the high value of the iodine number (96.18) points to a high content of carbon-carbon double bonds due to the high amount of unsaturated acids in WCO, producing high reactivity (Leung et al., 2010). The acidity value was significantly higher than those reported by López et al. (2015) and Rodriguez et al. (2017) (approximately 1.0%), representing a high content of free fatty acids in the WCO used in this research and also indicating a high degree of reusability (Alarcón et al., 2017). The exposure of the oil to moisture, high temperatures and oxygen for long periods of time, in addition to hydrolysis, causes the release of free fatty acids, leading then to a restriction in the biodiesel production process when an alkaline catalyst is used (Mohammadshirazi et al., 2014). On the other hand, as the acid value is higher than 1% the reaction should usually be performed in two stages, nevertheless,

as the MR of the mixture is low on WCO and free fatty acids, it is possible to perform the process without a neutralization stage (Helwani et al., 2009).

*Table 1. Results for WCO´s characterization.*

| Property | Waste cooking oil |
|---|---|
| Density (g/ml) | 0.931±0.02 |
| Acid value | 2.11±0.2 |
| Iodine (g/100g of substance) | 96.18±1.35 |
| Saponification (mg of KOH/g) | 208.21±1.07 |
| Humidity percentage (%) | 0.2 |
| Viscosity (cP) | 56.4±0.1 |

### 3.2 Response surface methodology (RSM) for biodiesel production

Based on the experimental results obtained, it was determined that all analyses will be carried out on samples taken ten minutes into the production process, as it was observed that by this time the mixture has fully reacted (data not shown). These results are similar to other reports where reaction times for hydrocavitation production using WCO were between 8 and 15 minutes (Chitsaz et al., 2018) (Chuah et al., 2017). Two response surface models (Figure 2) were developed for ECPKB and yield. The yield surface was adjusted to the model: $\text{YIELD} = 1.053 + 0.093\,\text{MR} - 0.291\,\text{KOH} - 0.0135\,MR^2 + 0.0178\,\text{MR} * \text{KOH}$ with $R^2 = 0.96$ and a p-value = 0.295. The ECPKB was adjusted to: $\text{ECPKB} = 167.4 - 32.4\text{MR} - 64.9\text{KOH} + 2.66MR^2 + 13.85\,\text{MR} * \text{KOH}$ with $R^2 = 0.985$ and a p-value = 0.183. The RSM models show a desirable correlation between the dependent and independent variables and a non-significant lack of fit, meaning that the model fulfills the acceptance criteria. According to the RSM, yield has an inversely proportional relationship with MR and KOH while ECPKB has a directly proportional relationship with both parameters.
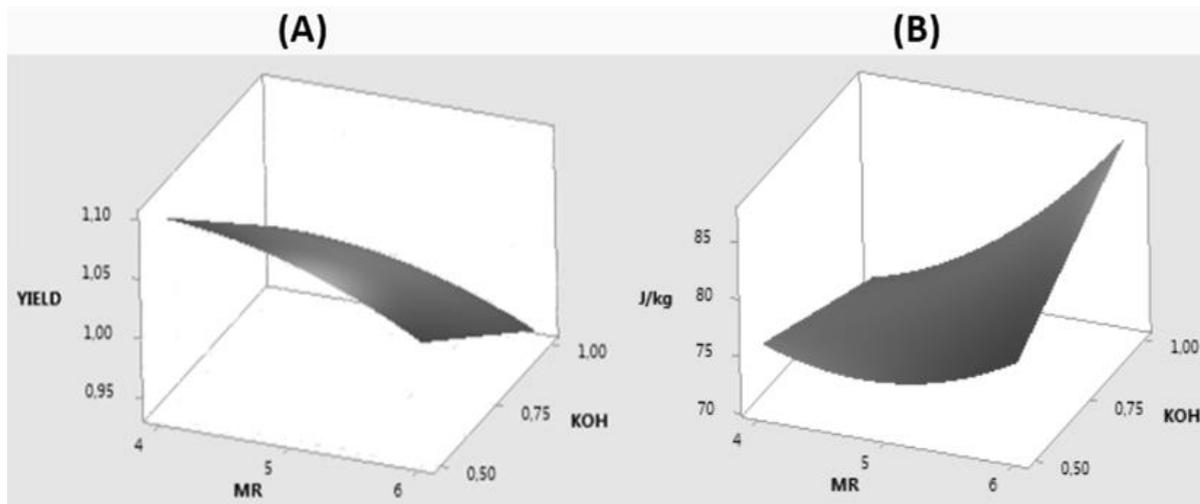


*Figure 2: (A) Surface plot obtained by RSM of MR and KOH versus YIELD. (B) Surface plot obtained by RSM of MR and KOH vs ECPKB.*

According to the adjusted models, an optimization was developed to maximize yield and minimize ECPKB resulting in (MR 4:1 and 0.5% KOH) as conditions to expect values of 1.09 for yield and 74.33 kJ/kg for ECPKB. A concentration lower than 0.5% KOH was evaluated (data not shown) but the yield was close to 0, so 0.5% was selected as the best, thus requiring the addition of catalyst for the transesterification reaction. Gogate (2008) achieved an experimental value of 296 kJ/kg ECPKB and a yield of 0.98 with a reaction time of 15 min under the following conditions: 4:4 ratio (w/v) of oil to alcohol, 1% of NaOH and a plate with 16 orifices, each with a diameter of 2 mm. Chuah et al (2017) reported 800 kJ/kg of ECPKB, 0.984 yield and a reaction time of 15 min under the following conditions: MR of 6:1, 1% of KOH, an inlet pressure of 2 bar and a reaction temperature of

60°C with a plate of 21 orifices, each with a diameter of 1 mm in a 50 liters reactor. In the current work, a considerably shorter reaction time of 10 min was obtained, indicating that the proposed operanting conditions for production resulted in a fast instigation of cavitation and, subsequently, faster conversion. This result could be explained by the higher acid value compared to other reports Lopez et al. (2015), Rodríguez et al. (2017), whereby the reaction between a monoglyceride and the methanol was easier.

*Table 2: Characterization of biodiesel obtained.*

| Molar relation | Percentage KOH % | Density Kg/m³ | Cetane Index | Calorific Value (kJ/kg) | Methyl esters % | Monoglicerides % | Diglicerides % |
|---|---|---|---|---|---|---|---|
| 6:1 | 1 | 854 | 50.5 | 39750 | 94.3 | 5.7 | 0 |
| 5:1 | 1 | 885 | 39.7 | 39520 | 97.4 | 1.2 | 1.2 |
| 4:1 | 1 | 870 | 51.3 | 39650 | 85.3 | 7.4 | 7.3 |
| 6:1 | 0.5 | 892.6 | 52.4 | 39250 | 86.3 | 2.2 | 8.6 |
| 5:1 | 0.5 | 883.7 | 55.3 | 39515 | 98.6 | 1.4 | 0 |
| 4:1 | 0.5 | 894.8 | 51.4 | 39250 | 83.2 | 2.4 | 8.1 |

Table 2 shows the biodiesel characterization results. According to this table, the main differences between results are in the percentage of methyl esters and cetane index. The maximum content of methyl esters was for 5:1 MR and 0.5% KOH (98.6%), with a cetane index of 55.3. These experimental conditions were different from the optimum point obtained in the RSM (4:1 MR and 0.5% KOH), where the methyl esters content was 83.2% and the cetane index was 51.4. For biodiesel production it is important to select conditions with the highest content of methyl esters, so we concluded the best conditions are 5:1 MR and 0.5% KOH. This aspect is an advantage for biodiesel production since the catalyst content is lower than previous reports our research group López et al. (2015), (Alarcón et al, 2017), (Rodríguez, 2017) during 10 minutes of reaction. In this condition, the ECPKB and yield were 69.119 kJ/kg biodiesel and 1.01, respectively, which are close to the optimum point from RSM.

On the other hand, soap could be produced during the reaction due to presence of fatty acids, but the intensity of the reaction and the washing process removed this soap (Talebian-Kiakalaieh et al., 2013). This process did not require two steps (acid and basic catalyst) to improve the yield reaction as reported (Pal et al., 2010), so it is a considerable advance in the biodiesel production from WCO.

## 4. Conclusions

RSM was a suitable technique for adjusting the experimental results. Although RSM predicted that the optimal parameters of production for both ECPKB minimization and yield maximization are 4:1 MR and 0.5% KOH, the biodiesel characterization showed that for this condition the reaction is not fully completed and it does not fulfill the minimum quality requirements for biodiesel, indicating that the optimal production value is 5:1 MR and 0.5% KOH considering the high quality of the product (98.6% of methyl esters, 55.3 of cetane index and 39515 kJ/kg). Finally, the low results on ECPKB, the high yield, the high product quality, the omission of preheating and mixing steps, the large decrease in reaction time and the reduction of the overall energy consumption justify the idea of bringing this process to an industrial level.

### Acknowledgments

### References

Alarcón, R., Malagón-Romero, D., Ladino, A., 2017, Biodiesel production from waste frying oil and palm oil mixtures, Chemical Engineering Transactions, 57, 571–576.

Bokhari, A., Chuah, L. F., Yusup, S., Klemeš, J. J., Kamil, R. N. M., 2016, Optimisation on pretreatment of rubber seed (Hevea brasiliensis) oil via esterification reaction in a hydrodynamic cavitation reactor, Bioresource Technology, 199, 414–422.

Chitsaz, H., Omidkhah, M., Ghobadian, B., Ardjmand, M., 2018, Optimization of hydrodynamic cavitation process of biodiesel production by response surface methodology, Journal of Environmental Chemical Engineering, 6(2), 2262–2268.

Chuah, L. F., Klemeš, J. J., Yusup, S., Bokhari, A., Akbar, M. M., Chong, Z. K., 2017, Kinetic studies on waste cooking oil into biodiesel via hydrodynamic cavitation, Journal of Cleaner Production, 146, 47–56.

Gogate, P. R., 2008, Cavitational reactors for process intensification of chemical processing applications: A critical review, Chemical Engineering and Processing: Process Intensification, 47(4), 515–527.

Helwani, Z., Othman, M. R., Aziz, N., Fernando, W. J. N., Kim, J., 2009, Technologies for production of biodiesel focusing on green catalytic techniques: A review, Fuel Processing Technology, 90(12), 1502–1514.

Khan, S., Siddique, R., Sajjad, W., Nabi, G., Hayat, K. M., Duan, P., Yao, L., 2017, Biodiesel Production From Algae to Overcome the Energy Crisis, HAYATI Journal of Biosciences, 24(4), 163-167.

Ladino, A., Herrera, J., Malagon-Romero, D., Prisciandaro, M., Piemonte, V., Capocelli, M., 2016, Biodiesel Production Via Hydrodynamic Cavitation: Numerical Study of New Geometrical Arrangements, Chemical Engineering Transactions, 50, 319–324.

Leung, D. Y. C., Wu, X., Leung, M. K. H., 2010, A review on biodiesel production using catalyzed transesterification, Applied Energy, 87(4), 1083–1095.

López, L., Bocanegra, J., Malagón-Romero, D., 2015, Obtención de biodiesel por transesterificación de aceite de cocina usado, Ingenieria y Universidad, 19(1), 155–172.

Maddikeri, G. L., Gogate, P. R., Pandit, A. B., 2014, Intensified synthesis of biodiesel using hydrodynamic cavitation reactors based on the interesterification of waste cooking oil, Fuel, 137, 285–292.

Moazeni, F., Chen, Y. C., Zhang, G, 2019, Enzymatic transesterification for biodiesel production from used cooking oil, a review, Journal of Cleaner Production, 216, 117–128.

Mohammadshirazi, A., Akram, A., Rafiee, S., Bagheri Kalhor, E., 2014, Energy and cost analyses of biodiesel production from waste cooking oil, Renewable and Sustainable Energy Reviews, 33, 44–49.

Pal, A., Verma, A., Kachhwaha, S. S., Maji, S., 2010, Biodiesel production through hydrodynamic cavitation and performance testing, Renewable Energy, 35(3), 619–624.

Rehan, M., Gardy, J., Demirbas, A., Rashid, U., Budzianowski, W. M., Pant, D., Nizami, A. S., 2018, Waste to biodiesel: A preliminary assessment for Saudi Arabia, Bioresource Technology, 250(November 2017), 17–25.

Rodríguez, D., Riesco, J., Malagon-Romero, D., 2017, Production of Biodiesel from Waste Cooking Oil and Castor Oil Blends, Chemical Engineering Transactions, 57, 679–684.

Sharma, A., Gogate, P. R., Mahulkar, A., Pandit, A. B., 2008, Modeling of hydrodynamic cavitation reactors based on orifice plates considering hydrodynamics and chemical reactions occurring in bubble, Chemical Engineering Journal, 143(1–3), 201–209.

Suresh, M., Jawahar, C. P., Richard, A., 2018, A review on biodiesel production, combustion, performance, and emission characteristics of non-edible oils in variable compression ratio diesel engine using biodiesel and its blends, Renewable and Sustainable Energy Reviews, 92(April 2017), 38–49.

Talebian-Kiakalaieh, A., Amin, N. A. S., Mazaheri, H., 2013, A review on novel processes of biodiesel production from waste cooking oil, Applied Energy, 104, 683–710.

Wu, P., Bai, L., Lin, W., Wang, X., 2018, Mechanism and dynamics of hydrodynamic-acoustic cavitation (HAC), Ultrasonics Sonochemistry, 49, 89–96.