Waste cooking oil as source for renewable fuel in Romania

F Um Min Allah¹, G Alexandru¹

¹Faculty of Mechanics, University of Craiova, Craiova, Romania

E-mail: fazaluminallah@hotmail.com

Abstract. Biodiesel is non-toxic renewable fuel which has the potential to replace diesel fuel with little or no modifications in diesel engine. Waste cooking oil can be used as source to produce biodiesel. It has environmental and economic advantages over other alternative fuels. Biodiesel production from transesterification is affected by water content, type of alcohol, catalyst type and concentration, alcohol to oil ratio, temperature, reaction rate, pH, free fatty acid (FFA) and stirrer speed. These parameters and their effect on transesterification are discussed in this paper. Properties of biodiesel obtained from waste cooking oil are measured according to local standards by distributor and their comparison with European biodiesel standard is also given in this paper. Comparison has shown that these properties lie within the limits of the EN 14214 standard. Furthermore emission performance of diesel engine for biodiesel-diesel blends has resulted in reduction of greenhouse gas emissions. Romanian fuel market can ensure energy security by mixing fuel share with biodiesel produced from waste cooking oil. Life cycle assessment of biodiesel produced from waste cooking oil has shown its viability economically and environmentally.

1. Introduction
Climate change and energy security are the main motives for using renewable energy resources [1]. Biodiesel is alternative fuel which can be defined as ethyl or methyl ester derived from vegetable oil or animal fats which can be used in diesel engine without or little modifications to diesel engines [2]. Vegetable oils are potential feedstock for biodiesel production [3]. Using vegetable oils for production of biodiesel reduces food security and costly as well [4], [5]. Price of waste cooking oil is lower than that of vegetable oils and diesel fuel [6].

Transesterification is the process in which animal fats or vegetable oils react with alcohols in the presence of a catalyst to glycerol and alkyl ester [7]. Chemical changes take place during frying of vegetable oil. Waste cooking oil contains free fatty acids and moisture content which have the ability to form soaps. Pre-treatment of waste cooking oil is necessary in order to prevent soap formation. The treatment consists of mechanical cleaning with water and chemical cleaning for removal of resins and deacidification. Solids and liquids are separated in the first phase. Liquid portion is heated up to 60°C which is then washed by water vapours at the temperature of 95 °C. Steam treatment can lead to lower peroxide value, acidity and water content of WCO. Water soluble impurities dissolve in water due to mixing and separated with the help of separator [8]. Biodiesel is purchased from local distributor Biomotor Prod. It has price of 4 lei/litre in Romania which is less than the price of diesel fuel in the market. This paper includes the factors affecting the production of biodiesel. Its physical and chemical properties lie within the standards of European biodiesel standard limits. Emission performance of diesel biodiesel blends is evaluated by using KDE 6500E diesel generator.
2. Transesterification
Vegetable oil is pre-treated with catalyst to form esters of free fatty acids (FFA) in order to eliminate saponification reaction. The reaction useful when raw material contains high content of FFA. Reaction is described in figure 1 and the factors affecting the transesterification reaction are also given below in equation 1 [9].

$$\text{Triglyceride} + 3 \text{HOCH}_2 \rightarrow 3 \text{CH}_2\text{OCOCR}_1 + \text{Catalyst} + \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{R}_1\text{COOCHR}_2$$

2.1. Water content
Water content in waste cooking oil reduces the amount of ester formation and accelerates the hydrolysis process. Water content should be less than 0.5% to attain 90% biodiesel and it is more critical for acid catalyzed reaction than base catalyzed reaction. Water is obtained as by-product when acid catalysts are used for esterification of FFA to form esters. Presence of water in biodiesel decreases efficiency of engine. Waste cooking oil can be heated up to 120°C to evaporate water and water vapours can be removed by anhydrous sodium sulphate or anhydrous magnesium sulphate. Presence of certain amount of water is required for some enzymes to be activated.

2.2. Type of alcohol
Methanol is used for biodiesel production in most of the cases as its recovery is easier from final product. Biodiesel yield from waste cooking oil is much higher by using methanol than other alcohols. Viscosity of biodiesel obtained is also lower by using methanol. Methanol is less costly but more toxic than ethanol. Azeotrope and water are formed when ethanol is used, making the separation of alcohol from water difficult during distillation. Some cases involve addition of i-butanol or t-butanol as solvent to avoid the inhibition of lipase by glycerol or methanol.

2.3. Catalyst type
Researchers have used various catalysts for the production of alkyl esters. It can be concluded that fastest catalyst is NaOH and among the catalysts used. Raw materials with higher FFA content, aid catalysts are used for transesterification. The problems related to the usage of homogeneous catalysts are soap formation and recovery of catalyst from final product. Research has shown that heterogeneous catalyst is not affected by FFA and moisture present in raw material. Enzyme catalytic reaction is slower than other catalytic reactions used for transesterification. The separation is easier for enzyme catalysts but preparation of enzyme catalyst is critical [10], [9].

2.4. Alcohol to oil ratio
Three moles of alcohol and one mole of triglyceride are needed to produce three moles of alkyl esters. Alcohol to oil ratio has positive effect on production of biofuel. Product formation rate increases as the concentration of reactant increases. Increase in molar ratio of alcohol to oil increases the product formation.

2.5. Free fatty acid (FFA)
Waste cooking oil has higher content of FFA than fresh cooking oil. Higher FFA content will lead to formation of water and soap. Transesterification process will not proceed if FFA content exceeds 3% even with homogeneous base catalyst. The problem can be solved by using heterogeneous catalyst or by pre-treatment with homogeneous or heterogeneous acid catalyst for esterification of FFA to form free fatty acid esters. Rate of acid catalyzed reaction is low and soaps formed during neutralization of FFA by using base catalyst can be converted into FFA by adding phosphoric acid.
2.6. Temperature
There is significant effect of temperature on transesterification. Increase in temperature increases biodiesel yield and reaction rate. Temperature shouldn’t exceed the boiling point of alcohol to avoid evaporation of alcohol. Viscosity of biodiesel will increase if temperature is maintained below 50°C. Waste cooking oil is heated up to 120°C in order to remove water and then cooled up to 60°C. Highest biodiesel yield was recorded at 65°C for waste cooking oil by using KOH catalyst.

2.7. Reaction time
Reaction time depends upon the availability of reactants and 99% of yield can be obtained if reaction is carried out for longer period. Reaction time has an impact on the properties of biodiesel. The reaction time should be optimized in order to maximize yield and minimize the production cost.

2.8. pH
It isn’t the major factor while using acid or base catalyst but it can be considered during the usage of lipase as catalyst because enzyme can be decomposed at lower or higher pH values.

2.9. Stirrer speed
Proper mixing of reactants is necessary for completion of transesterification reaction. Agitation increases the rate of reaction as well as diffusion of reactants and catalyst into each other. Optimizing the stirrer speed is necessary to obtain maximum yield.

2.10. Catalyst concentration
High temperature conditions are required for the conversion of waste cooking oil into renewable fuel without using catalyst. Biodiesel yield increases with the increase in concentration of catalyst. However conversion rate decreases with the increase in catalyst concentration maybe due to increase in viscosity of mixture. Optimum concentration of catalyst may vary with type of raw materials and catalysts [11].

3. Biodiesel properties
Physical and chemical properties of fuel are important in determining its quality. Biodiesel is purchased from local distributor Biomotor Prod. Biodiesel is produced from waste cooking oil of canola and soybean cooking oils. Physical and chemical properties are measured according to local standards with the help of supplier and Faculty of Chemistry. A comparison of European biodiesel standard and properties of biodiesel obtained from waste cooking oil is given in table 1.

| Properties                          | Test Method       | Biodiesel from waste cooking oil | EN-14214 |
|-------------------------------------|-------------------|---------------------------------|----------|
| Density(kg/m³) @ 25°C               | SR EN ISO 3657    | 887.6                           | 860–900  |
| Kinematic viscosity(cSt) @ 40°C     | ASTM D-445        | 4.5                             | 3.5–5    |
| Iodine value (mgIod/g)              |                   | 94                              | <120     |
| Flash point (°C)                    | EN SR ISO 5489: 2009 | 159                           | >101     |
| Saponification value (mgKOH/g)     | SR EN ISO 3657: 2005 | 189                           |          |
| Acid value (mgKOH/g)                |                   | 0.32                            |          |
4. Emission performance

KDE 6500E diesel engine is selected in order to evaluate the emission performance of biodiesel-diesel blends. B10, B20 and B30 blends are used for performance evaluation of diesel generator. Carbon dioxide, hydrocarbon and carbon monoxide emissions for diesel fuels and blends can be seen in figure 2, figure 3 and figure 4. Experimental layout can be seen in figure 1 while specifications of diesel engine are summarized in table 2.

Figure 1. Experimental layout [12], [13].

(1-Heat exchanger, 2- Ventilator, 3 and 4- Flow pipe, 5- Oil reservoir, 6- Oil pump, 7- Electric resistances, 8- Control board, 9- Adjustable auto transformer, 10- Voltmeter and ammeter, 11- Power cable, 12- Battery, 13- Electric generator, 14- Fuel tank, 15- Transmission, 16- Diesel engine, 17- Exhaust pipe, 18- Measurement cable, 19- Cable, 20- exhaust gas probe, 21- oil temperature sensor and 22- Exhaust gas analyzer).

Table 2. Specification of diesel generator KDE 6500E.

| Properties                  | KM186FA                     |
|-----------------------------|-----------------------------|
| Rated speed                 | 3000rpm                     |
| Engine type                 | Single cylinder, vertical, four stroke, direct injection |
| Cooling system              | With air                    |
| Compression ratio           | 19:1                        |
| Electromotor capacity       | 2V/0.88kW                   |
| Rated frequency             | 50Hz                        |
| Rated voltage               | 230V                        |
| Rated current               | 39.2A                       |
| Maximum Power output        | 5kVA                        |
| Rated frequency             | 50Hz                        |
Figure 2. Carbon Dioxide emissions.

Figure 3. Unburned hydrocarbon emissions.

Figure 4. Carbon monoxide emissions.
5. Life cycle of biodiesel from waste cooking oil
Biodiesel produced from waste cooking oil is considered sustainable as it is produced from waste recyclable product. Ozata et al. compared life cycles of biodiesels produced from rapeseed oil and waste cooking oil. They concluded that biodiesel produced from waste cooking oil is better option for vehicles in Istanbul [14]. Process of biodiesel production from waste cooking oil is depicted in figure 5.

Chua et al. conducted life cycle assessment of biodiesel production from waste cooking oil in Singapore. They concluded that biodiesel production and usage in vehicles are most energy efficient than usage of diesel fuel. Biodiesel has the potential to replace diesel fuel. Furthermore, production of biodiesel from waste cooking oil has environmental advantage over its disposal. Recycling waste cooking oil has not only environmental benefits but it provides economic benefits to the users of cooking oil and food establishments which further ensures the supply of waste cooking oil [16]. Romanian food industry uses sunflower and canola oil for cooking purposes. Used cooking oil can be obtained at lower price. There are number of biodiesel producers on industrial scale in Romania. Research carried out by Sauciuc et al. in Romania also suggested that biodiesel obtained from waste cooking oil has better physical and chemical properties than that of diesel fuel [17]. Production and quality may vary with supplier but they must comply with European biodiesel standard EN 14214.

Decrease in emissions is noted by using diesel-biodiesel blends in KDE 6500E diesel generator.

6. Conclusions
Biodiesel production from waste cooking oil ensures supply of sustainable and renewable fuel. Water content, alcohol type, alcohol to oil ratio, catalyst type and concentration, free fatty acids, reaction time, pH, stirrer speed and temperature are the parameters which have great impact on transesterification process. Comparative analysis of physical and chemical properties was carried out which concluded that the properties of biodiesel obtained from waste cooking oil lie within the limits of European biodiesel standard EN 14214. Emission performance of diesel engine for diesel-biodiesel blends have shown following results. Increase in CO₂ emissions is recorded with increasing load but decrease in emissions is recorded with increase in concentration of biodiesel in blends. Hydrocarbon emissions are recorded lower for higher loads and higher biodiesel concentrations of biodiesel in blends. Carbon monoxide emissions were lower for higher loads while decrease in CO emissions are recorded with higher concentration of biodiesel in blends. Biodiesel produced from waste cooking oil has economic and environmental benefits over conventional fuels. Romania has existing infrastructure for production and usage of biodiesel from waste cooking oil. Furthermore, it can be concluded that energy share of biodiesel in fuel market helps in achieving EU emission targets as well as to fulfil Kyoto protocol limitations.
7. References

[1] Lackner K S 2010 Comparative impacts of fossil fuels and alternative energy resources *Issues in Environmental Science and Technology (Carbon capture: Sequestration and storage)* 29 (Royal society of Chemistry- Springer)

[2] Predojevic Z J 2008 The production of biodiesel from waste frying oils: A comparison of different purification steps *Fuel* 87 pp 3522-3528

[3] Issariyakul T and Dalai A K 2014 Biodiesel from vegetable oils *Renewable and Sustainable Energy Reviews* 31 pp 446-471

[4] Karmee S K, Liardi D, Lee J and Lin C S K 2015 Conversion of lipid from food waste to biodiesel *Waste Management* 41 pp 169-173

[5] Koizumi T 2015 Biofuels and food security *Renewable and Sustainable Energy Reviews* 52 pp 829-841

[6] Phan A N and Phan T M 2008 Biodiesel production from waste cooking oils *Fuel* 87 pp 3490-3496

[7] Rabu R A, Janajreh I and Honnery D 2013 Transesterification of waste cooking oil: process optimization and conversion rate evaluation *Energy Conversion and Management* 65 pp 764-769

[8] Banerjee A and Chakraborty R 2009 Parametric sensitivity in transesterification of waste cooking oil for biodiesel production: A review *Resources, Conservation and Recycling* 53 pp 490-497

[9] Ejikeme P M and Anyaogu I D 2010 Catalysts in biodiesel production by transesterification process- An insight *E-Journal of Chemistry* 7(4) pp 1120-1132

[10] Thanh L T, Okitsu K, Boi L V and Maeda Y 2012 Catalytic technologies for biodiesel fuel production and utilization of glycerol *Catalysts* 2 pp 191-222

[11] Ganaprakasam A, Sivakumar V M, Surendhar A, Thirumarimurugan M and Kannadasan T 2013 Recent strategy of biodiesel production from waste cooking oil and process influencing parameters: A review *Journal of Energy* pp 1-10

[12] Tutunea D, Marin B, Ilie D and Alexandru D 2016 Study of emission of a mono cylindrical diesel engine fuelled with biodiesel of palm oil *Applied Mechanics and Materials* 823 pp 297-302

[13] Um Min Allah F and Alexandru G 2016 Experimental investigation on the effect of bioethanol on emission performance of diesel engine for rapeseed biodiesel-diesel blends *Applied Mechanics and Materials* 823 pp 319-322

[14] Ozata I, Ciliz N, Mammadov A, Basak B and Ekinci E 2009 Comparative life cycle assessment approach for sustainable transport fuel production from waste cooking oil and rapeseed available on https://gin.confex.com/gin/2009/webprogram/Paper2602.html

[15] Information available on: http://www.biofuels.coop/education/resources/energy-balance

[16] Chua C B H, Lee H M and Low J S C 2010 Life cycle emissions and energy study of biodiesel derived from waste cooking oil and diesel in Singapore *International Journal of Life Cycle Assessment* 15 pp 417-423

[17] Sauciu A, Dumitrescu L, Manciulea I and Zaha C 2011 Studies on recycling of waste cooking oils for biodiesel production *Environmental Engineering and Management journal* 10(2) pp 205-211

Acknowledgement

Experiments are conducted with the help of laboratory staff at University of Craiova. Their cooperation in conducting the experiments is acknowledged.