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Effects on Activation Energy and Emissions of Diesel Fuel by the Addition of Biodiesel, Di-*tert*-butyl Peroxide as an Additive and Hydrogen as Gaseous Fuel in a Diesel Engine

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ABSTRACT

Biofuels along with fossil fuels are vital energy resources, and their production and use have grown significantly worldwide. This study focuses on the effect of activating energy on diesel fuel emissions by adding biodiesel (Karanja oil), Di-*tert*-butyl peroxide (DTBP) as an additive, and hydrogen as a gaseous fuel in a diesel engine. Activation energy is determined using the mathematical relation of cetane number and experimental data from various fuel property measurements. With the addition of 1% DTBP as a catalyst or additive in pure diesel, a diminishment in the energy activation was observed to be 0.90% with a decrease in the nitrogen oxide (NO_x), unburnt hydrocarbon (HC), carbon dioxide (CO_2) and carbon monoxide (CO) emissions, decreasing the vibration in the diesel engine.

Keywords: Diesel; Biodiesel of Karanja oil; Di-*tert*-butyl peroxide; Hydrogen fuel.

1. INTRODUCTION

Decreasing oil reserves has significantly impacted environmental awareness, leading to a growing interest in renewable energy sources. As a result, renewable energy sources are expanding considerably. Vegetable oils undergo a transesterification reaction to produce biodiesel, which is one of the key renewable energy sources for diesel engines. Biodiesel is a non-toxic, biodegradable, and renewable fuel that offers many advantages compared to traditional diesel fuels. It can be used either neat or as a blend with petroleum diesel fuels. Biodiesels contain 10-12% oxygen by weight and are free from sulfur and aromatic compounds. The particulate emissions, hydrocarbons (HC), and carbon monoxide (CO) produced by biodiesel-fueled engines are significantly lower than those produced by engines running on petroleum diesel (Graboski and McCormick, 1998; Tomasevic and Siler-Marinkovic, 2003). Additionally, biodiesel improves engine lubricity, which contributes to longer component life (Gerpen, 2005). Improvement in the combustion step during the determination of biodiesel composition has been attempted to a significant extent by various researchers. During combustion, it was observed that biodiesel exhibits fuel properties that play a crucial role in its performance. One such property is the cetane number (CN), which significantly influences combustion and engine performance. The CN is commonly used as an indicator to determine the ignition quality of diesel fuel. Parameters such as the CN are utilized to assess biodiesel quality, particularly in compression ignition (CI) engines, where the fuel ignition delay time is directly proportional to the cetane number of biodiesels (Knothe *et al*. 2003). Several performance features, such as heating value and density, have also been found to correlate with the CN of biodiesel (Lakshmi et al. 2020).

There is a growing global trend toward the use of biofuels in engines (Henein 1976). Thermal processes produce several pollutants, including nitrogen oxides (NOx), HC, CO, CO_2, and particulate matter (PM). The formation of these pollutants is influenced by the properties of the fuel, such as activation energy, cetane number, and density, as well as engine parameters like injection timing, bore, stroke, and compression ratio (Saravanan *et al*. 2012; Conconi and Crnkovic, 2013). These emissions can harm the environment and living beings; hence, they must be carefully evaluated when introducing new technologies or fuels (Bowman, 1979). Precursors to several natural and environmental issues include nitrogen oxides (NOx), which contribute to problems such as global warming, acid rain, ozone layer depletion, and photochemical smog. Combustion pollutants primarily come from two sources: stationery and mobile sources. CO_2 emissions have a significant environmental impact, with global warming and the greenhouse effect being driven by gases such as NOx, CO_2, CO, and HC. The use of fossil fuels in internal combustion (IC) engines is a major source of CO_2

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emissions. To reduce emissions of various gases, the use of renewable energy sources can be increased; additionally, plant photosynthesis contributes to CO_2 emissions through the combustion process, but this is offset by absorption (Henein, 1976).

The current study investigates the effects on energy activation and emissions of various gases such as NOx, CO_2, CO, and HC by adding biodiesel (Karanja oil) with Di-*tert*-butyl peroxide as an additive, and hydrogen as a gaseous fuel in IC engines. Furthermore, the research explores the effects of activation energy on cetane number and the vibrations of IC engines.

2. MATERIALS AND METHODS

2.1 Measurement of Fuel Properties

The standard methods were used for the determination of the physical as well as chemical properties of biodiesel of Karanja oil (BKO). The essential properties of diesel, and biodiesel of Karanja oil and their blends have been measured by experimental methods.

2.1.1 Viscosity

Viscosity is a measure of a fluid's resistance to flow, caused by internal friction within the fluid. In the case of oil, its resistance to flow decreases as temperature increases, allowing the oil to flow more easily. This reduction in viscosity with rising temperature facilitates finer droplet formation and improves pumping and atomization processes. Viscosity was measured using Redwood viscometers, where the Redwood viscosity value is defined as the time required for 50 milliliters of oil to flow through the viscometer at a specified temperature.

2.1.2 Calorific Value

The calorific value represents the amount of thermal energy released per unit quantity of fuel during complete combustion. It is an essential parameter for assessing the suitability of Karanja oil biodiesel (BKO) as an alternative to diesel fuel. The calorific value of vegetable oil methyl esters was determined using a bomb calorimeter, following the standard ASTM D240 procedure.

2.1.3 Flash and Fire Point

The flash point is the minimum temperature at which a fuel, such as biodiesel, produces sufficient vapor to ignite. It is inversely proportional to the volatility of the fuel and plays a significant role in determining its fire safety. A minimum flash point is necessary to ensure the safe handling of diesel fuel. The flash points of the samples were measured using an automated Pensky-Martens closed cup apparatus, within the 60 - 190 °C temperature range.

2.1.4 Relative Density

Relative density is defined as the mass of a liquid per unit volume at a given temperature. It is a critical property of biofuels. The density of the biodiesel was measured at 312 K using a pycnometer.

2.1.5 Cetane Number

The cetane number (CN) of a fuel is a key indicator of its chemical and physical properties, particularly in determining ignition delay. A higher cetane number corresponds to shorter delay times and smoother engine performance. Biodiesel, with its higher oxygen content compared to diesel, typically exhibits a higher cetane number. For Karanja oil biodiesel, a mathematical relationship was developed to determine the cetane number, as shown in Equation (1). The constants K_1, K_2, K_3, K_4, and K_5 were calculated using a multiple linear regression model.

$$CN = k_5 + K_4 \nu + k_3 HV + k_2 FP + K_1 \rho \quad \ldots (1)$$

$CN = 98.01 - 0.04\nu - 0.359HV + 0.082FP - 43.077\rho$

Where, HV, FP, and ρ are viscosity, heating value, flash point, and density having units as mm^2/sec, MJ/sec, °C, and kg/l respectively, as presented in Table 1. Therefore, the mathematical equation shows that apparent activation energy (E_a) decreases (Table 3) with increasing fuel cetane number, as shown in Equation (2):

$$E_a = (618840)/(CN) + 25 \quad \ldots (2)$$

Table 1. Fuel properties

Item (%)	Density at 25 ˚C (kg/m^3)	Lower Calorific Value (MJ/kg)	Flash Point (˚C)	Kinematic Viscosity @ 40 ˚C (mm^2/sec)
D100	0.818	41.33	51	2.09
B100	0.885	36.94	68	5.31
DTBP	0.787	35.38	6	1.36
D-99 + DTBP-1	0.817	38.69	50	2.81

Table 2. Standard test methods and Measurement devices for various properties of Diesel fuel

Property	Standard test method	Measurement device
Viscosity	ASTM D445	Redwood viscometer
Calorific value	ASTM D240	Bomb calorimeter
Flash and fire point	ASTM D42	Pensky Martens apparatus
Density	ASTM D287	Hydrometer

Table 3. Activation energy (E_a) with calculated value of cetane number and different percentages of items

Item (%)	Cetane number	E_a (j/mol)
DTBP100	51.84	8054
B100	51.98	8039
D100	52.1	8026
D-99 + DTBP-1	52.914	7942
H_2	0	24753.6

Table 4: Activation energy (E_a) with the experimental emission value of various gases and their vibrations and different percentages of items

Item (%)	E_a j/ mol	NO_x ppm	HC ppm	CO_2 (%)	CO (%)	Vibration Hz
D100	8026	2071	25	7.4	0.22	3105
B100	8039	932	16	5.2	0.17	2630
DTBP100	8054	1724	22	5.1	0.16	2682
D-99+ DTBP-1	7954	1786	26	6.1	0.18	2226

3. RESULT AND DISCUSSION

3.1 Activation Energy and Cetane Number in Diesel/Biodiesel Engine

In Fig. 1, for a diminishment in the activation energy (0.27%) an increase in the cetane number of pure biodiesels of Karanja oil (BKO) was observed to be 0.186 %, compared to pure DTBP. Moreover, diminishment in the activation energy of pure diesel and 99% diesel with 1% DTBP were observed to be 0.35% and 1.39% respectively (Table 3). Cetane number increases due to enhancement in the fuel properties such as viscosity, calorific value, fire point, and relative density because of diminishment in the activation energy. The slope and intercept were obtained from Equation (3) using linear fitting (regression):

$$CN = -0.0096E_a \text{ (J/mol)} + 129.26 \qquad \dots (3)$$

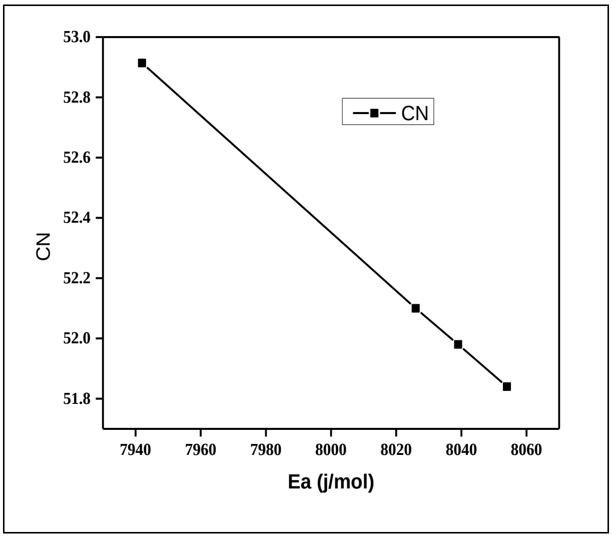

Fig. 1: Cetane number vs. Activation energy

3.2 Activation Energy and Emission in Diesel/ Biodiesel Engine

In Fig. 2, for the increment in the activation energy (0.16%), a decrease in the NO_x emission of biodiesel of BKO was observed to be 16.17% as compared to pure diesel. This results from the vaporous fuel's slow-burning rate when CO_2 is present in BKO, and CO_2 brings down the intake fluid's oxygen content. Contrary to diesel fuel, adding BKO raises the working fluid's particular warm capacity, which moderates the fire spread and brings down the combustion temperature during the combustion route (Selim *et al*. 2008; Mustafi *et al*. 2013). Moreover, for the increment of the activation energy of pure DTBP (0.35%), a decrease in the NO_x emission was observed to be 0.35% as compared to pure diesel (Table 4). However, when the addition of 1% DTBP as a catalyst or additive in diesel (D100) undergoes diminishment in the activation energy was observed to be 0.90% as compared to pure diesel, a decrease in the NO_x emission. The slope and intercept were obtained in Equation (4) using linear fitting (regression) as follows:

$$NO_x\left(ppm\right) = -0.0275Ea\left(j/mol\right) + 8162.94 \qquad \dots (4)$$

As shown in Fig. 3, for an increment in energy activation (0.16%), a decrease in HC emission of BKO was observed to be 40% as compared to pure diesel because of its decreased oxygen content by weight and low cetane value, which promotes worse combustion in the combustion chamber; BKO emits more greenhouse gases. Moreover, for an increment in the activation energy of pure DTBP (0.35%), a decrease in the HC emission was observed to be 10% as compared to pure diesel. Finally, when the addition of 1% DTBP as a catalyst or additive in pure diesel undergoes diminishment in the energy activation (0.90%), a decrease in HC emission was observed to be 0.89% as compared to pure diesel (Table 4). The slope and intercept were obtained in equation (5) using linear fitting (regression) as follows:

$$HC\ \left(ppm\right) = -6.638Ea\left(j/mol\right) + 8162.94 \qquad \dots (5)$$

In Fig. 4 and 5, an increment in the activation energy (0.16%) decreased CO_2 and CO gases; emissions of BKO of these gases were observed to be 29.72% and 22.72% respectively, as compared to pure diesel. Since biodiesel fuel has an oxygen substance of generally 11% by weight, it experiences complete combustion and diminishes the plausibility of incomplete combustion, resulting in lower concentrations of emission of CO. The lower oxygen concentration of biodiesel often prevents as much CO from being converted to CO_2. Biodiesel has a closed carbon life cycle, where the CO_2 emissions released during its use are recycled and absorbed by growing plants. Moreover, for an increment in the activation energy of pure DTBP (0.35%), a decrease in the emissions of CO_2 and CO gases was observed to be 31.08% and 27.27% respectively, as compared to pure diesel. Finally, when the addition of 1% DTBP as a catalyst or additive in pure diesel undergoes diminishment in the activation energy (0.90%), there were reductions in the CO_2 and CO gas emissions as compared to pure diesel (Table 4). The slope and intercept were obtained in Equations (6) and (7) using linear fitting (regression) as follows:

$$CO_2(\%) = -13.53Ea(j/mol) + 8095.78 \quad \dots (6)$$

$$CO\,(\%) = -280.72Ea(j/mol) + 8066.48 \quad \dots (7)$$

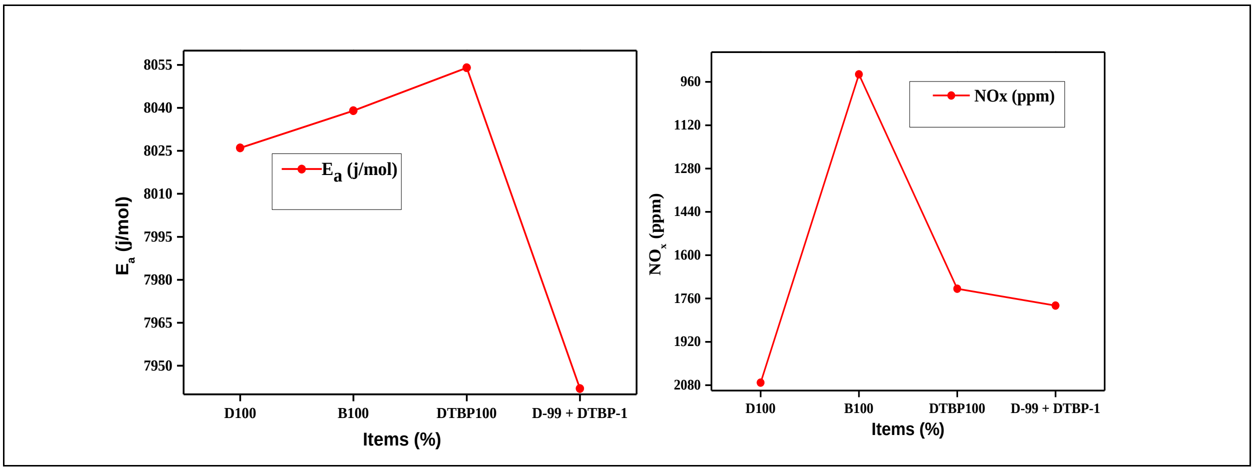

Fig. 2: Activation energy vs. different percentage of items along with NO_x emission

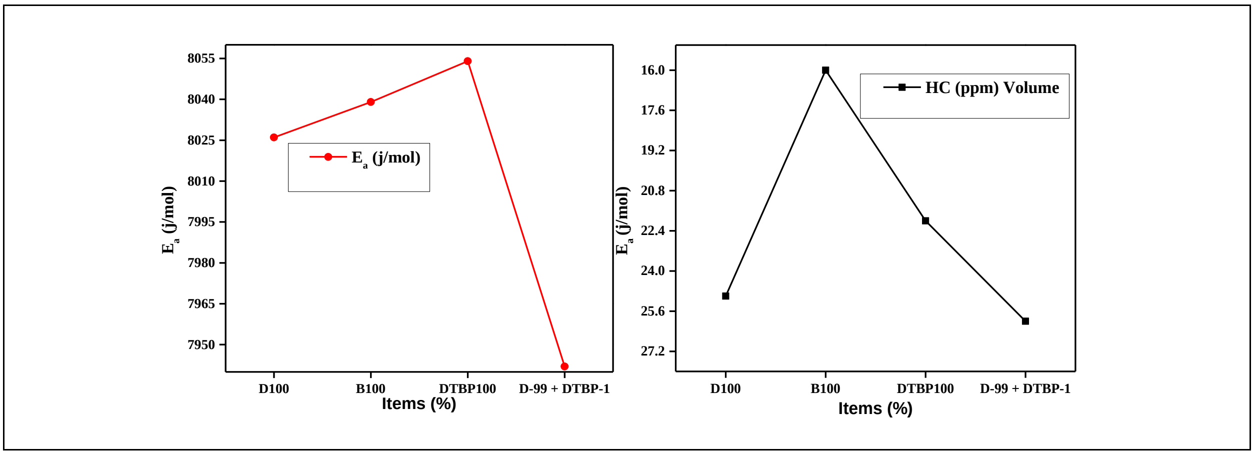

Fig. 3: Activation energy vs. different percentage of items along with HC emission

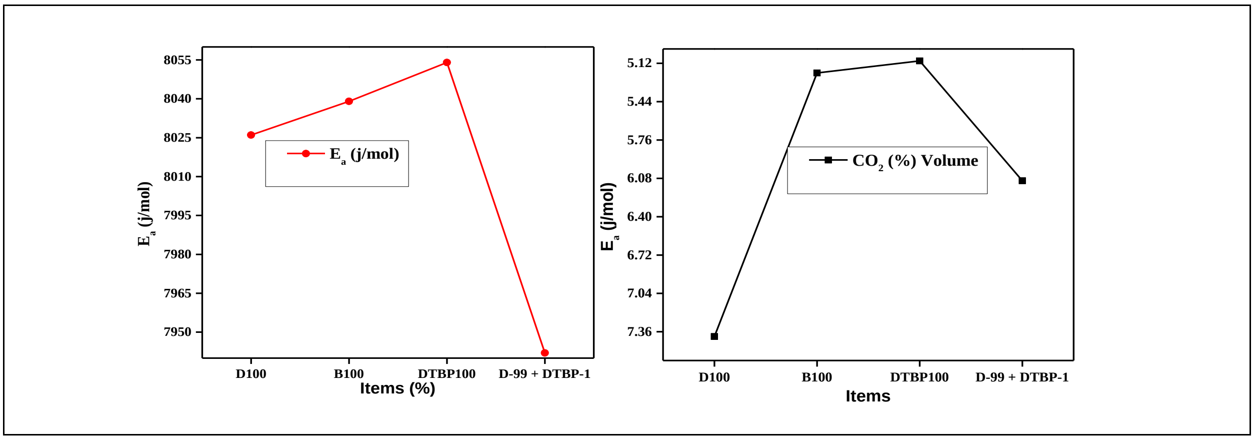

Fig. 4: Activation energy vs. different percentage of items along with CO_2 emission

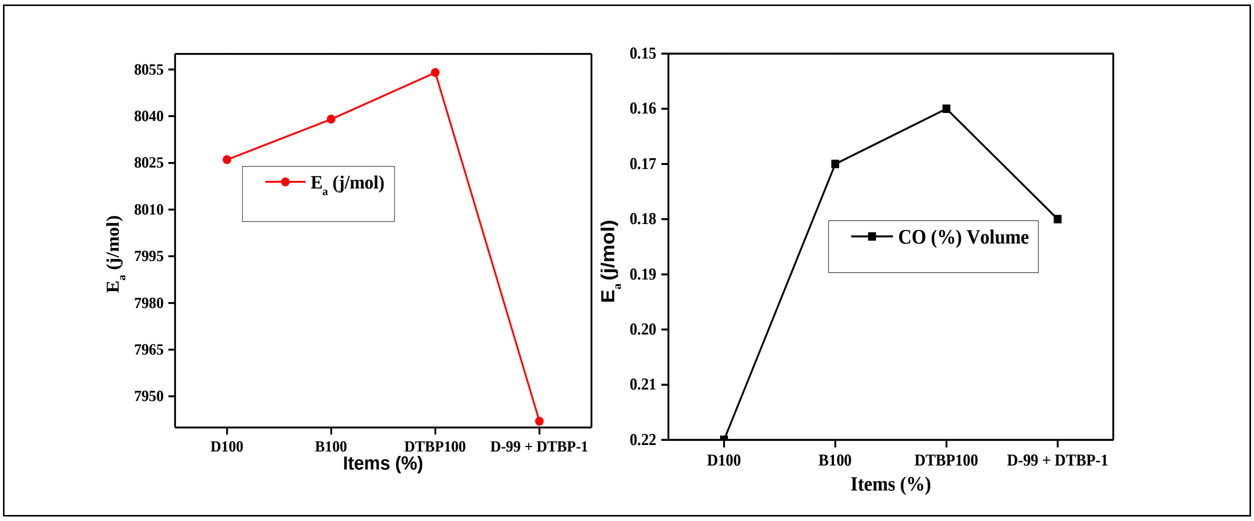

Fig. 5: Activation energy vs. different percentage of items along with CO emission

4. CONCLUSION

1. The diminishment in the activation energy of pure diesel (D100) and D-99% + DTBP-1% were observed to be 0.35% and 1.39% respectively.

2. The addition of 1% DTBP as a catalyst or additive in diesel fuel undergoes diminishment in the activation energy was observed to be 0.90% with decreasing the NO_x, HC, CO_2, and CO emissions as compared to pure diesel fuel.

3. The addition of 1% DTBP as a catalyst or additive in pure diesel undergoes diminishment in the activation energy was observed to be 0.90% with decreasing the vibration in a diesel engine as compared to pure diesel fuel.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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REFERENCES

Bowman, C. T., Kinetics of Pollutant Formation and Destruction in Combustion, *Energy and Combustion Science*, *Elsevier*, 35–47 (1979). https://doi.org/10.1016/B978-0-08-024780-9.50007-1

Conconi, C. C. and Crnkovic, P. M., Thermal behavior of renewable diesel from sugar cane, biodiesel, fossil diesel and their blends, *Fuel Process. Technol.*, 1146–11 (2013). https://doi.org/10.1016/j.fuproc.2013.03.037

Gerpen, J. V., Biodiesel processing and production, *Fuel Process. Technol.*, 86(10), 1097–1107 (2005). https://doi.org/10.1016/j.fuproc.2004.11.005

Graboski, M. S. and McCormick, R. L., Combustion of fat and vegetable oil derived fuels in diesel engines, *Prog. Energy Combust. Sci.*, 24(2), 125–164 (1998). https://doi.org/10.1016/S0360-1285(97)00034-8

Henein, N. A., Analysis of pollutant formation and control and fuel economy in diesel engines, *Prog. Energy Combust. Sci.*, 1(4), 165–207 (1976). https://doi.org/10.1016/0360-1285(76)90013-7

Knothe, G., Matheaus, A. C. and Ryan, T. W., Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester, *Fuel*, 82(8), 971–975 (2003). https://doi.org/10.1016/S0016-2361(02)00382-4

Lakshmi, N. V., Rao, L. B. and Devireddy, S. B. R., Effect of Fiber Percentage and Stacking Sequence on Mechanical Performance of Unidirectional Hemp and Palmyra Reinforced Hybrid Composites, *Rev. Compos. Matér. Avancés*, 30(3–4), 153–160 (2020). https://doi.org/10.18280/rcma.303-405

Mustafi, N. N., Raine, R. R. and Verhelst, S., Combustion and emissions characteristics of a dual fuel engine operated on alternative gaseous fuels, *Fuel*, 109669–678 (2013). https://doi.org/10.1016/j.fuel.2013.03.007

Saravanan, S., Nagarajan, G. Anand, S., and Sampath, S., Correlation for thermal NOx formation in compression ignition (CI) engine fuelled with diesel and biodiesel, *Energy*, 42(1), 401–410 (2012). https://doi.org/10.1016/j.energy.2012.03.028

Selim, M. Y. E., Radwan, M. S. and Saleh, H. E., Improving the performance of dual fuel engines running on natural gas/LPG by using pilot fuel derived from jojoba seeds, *Renew. Energy*, 33(6), 1173–1185 (2008). https://doi.org/10.1016/j.renene.2007.07.015

Tomasevic, A. V. and Siler-Marinkovic, S. S., Methanolysis of used frying oil, *Fuel Process. Technol.*, 81(1), 1–6 (2003). https://doi.org/10.1016/S0378-3820(02)00096-6