Production of Biodiesel from Non-Edible Oil and effect of blending with diesel on fuel properties

M.Abdel fatah*
Petrochemical .Department
Faculty of Engineering
Pharos University
Alexandria, Egypt
*Corresponding Author: E-mail: marwa.abdelfattah@pua.edu.eg

H.A. Farag
Chemical Engineering Department
Faculty of Engineering
Alexandria University
Alexandria, Egypt

M.E. Ossman
Petrochemical .Department
Faculty of Engineering
Pharos University
Alexandria, Egypt

***ABSTRACT* – Biodiesel is gaining more and more importance as an attractive fuel due to the depleting fossil fuel resources. Chemically biodiesel is mono alkyl esters of long chain fatty acids derived from renewable feed stock like edible oils and non edible oils. This paper discusses the production of biodiesel from Egyptian jojoba oil by transesterification with methanol in presence of an alkaline catalyst (KOH) to give the corresponding mono alkyl esters. The variables affecting the yield of the biodiesel produced were studied. The variables investigated were reaction time (0.5–3 .5h), catalyst concentration (0.3–2wt %), temperature (20-65 ˚C) and methanol: oil molar ratio (3:1–10:1). From the results obtained, the best yield percentage was obtained using a methanol: oil molar ratio of 6:1, KOH as catalyst (0.5%) and 60 ± 1 ºC temperature for 3 h. The true yield of biodiesel was determined according to GC-MS. From the results it was clear that the produced biodiesel fuel was in the recommended standards range of biodiesel fuel. Numerical correlation using regression analysis for the true yield of biodiesel produced in terms of the operating conditions of the transesterification process was presented. Finally, some biodiesel properties have been done and compared with pure diesel.**

Key words: biodiesel; transesterification; jojoba oil; alternative fuel; fuel properties.

I. INTRODUCTION

The demand for energy around the world is increasing; specifically the demand for petroleum fuels that is rapidly becoming scarcer and more expensive [1]. It is anticipated that the petroleum demand will increase from 84.40 million barrels to 116.00 million barrels per day by 2030 in USA alone [2, 3]. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels while petroleum-based products are one of the main causes of anthropogenic carbon dioxide (CO2) emissions to the atmosphere. One-fifth of global CO2 emissions are created by the transport sector [4], which accounts for some 60% of global oil consumption [5].The scientific community was forced to investigate new types of renewable energy sources, mainly because of the greenhouse effect brought about by the growing usage of fossil fuels and thus to increase the time over which fossil fuels will still be available [6]. Biodiesel is considered to be a possible substitute for conventional diesel. There are a great number of advantages for using biodiesel specifically it is biodegradable, non-toxic, renewable and has reduced emission of CO, SO2, particulate matter, volatile organic compounds and unburned hydrocarbons as compared to conventional diesel [7,8],also it has higher cetane number and flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel [9].

Various oils have been in use in different countries as raw materials for biodiesel production owing to its availability. In the USA and Europe, the surplus edible oils like soybean oil, sun flower oil, and rapeseed oil are being used as feedstock for the production of biodiesel [10]. However, the viscosity of vegetable oil is several times higher than that of mineral diesel due to their large molecular mass and

chemical structure [11]. More than 95% of biodiesel production feedstock's come from edible oils. Although they are mainly produced in many regions; it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [12]. Moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, non edible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care [13, 14].

Numbers of methods are currently available and have been adopted for the production of biodiesel fuel. The most commonly used method for converting oils to biodiesel is through the transesterification of animal fats or edible and non-edible oils. [15-19]. It has many advantages over other processes e.g., it is performed under normal conditions and it returns good yield of better quality biodiesel [20,21].The rate of yield of biodiesel via transesterification depends upon many parameters. The most important of which are amount and type of alcohol, amount and type of catalyst, the reaction temperature, and reaction time. [22, 23]

The search for alternative fuels has lead researchers to investigate more sustainable sources such as, jojoba oils. This oil is rare in that is an extremely long (C26–C48) straight chain wax ester, and not a triglyceride, making jojoba and its derivative jojoba esters more similar to sebum and whale oil than traditional vegetable oils [24]. Pure jojoba oil has been also used and its blends with diesel fuel for diesel engines [25]. This research is concerned with producing biodiesel from non edible oil (Egyptian jojoba oil). The choice of the Egyptian jojoba oil (GREEN GOLD) is due to its availability in Egypt [26] , low prices (0.8 €/kg) [27], low chemical reactivity and very high boiling point (382˚C) that gives this product very important physico-chemical properties and uses [28] .

The aim in this work is study the Egyptian jojoba oil (Green Gold) as an application of non-edible oil for biodiesel production using methanol and potassium hydroxides as a catalyst, and to study the different variables affecting the alkaline catalysis process of Egyptian jojoba oil, namely reaction time, methanol: oil molar ratio, temperature, percentage of alkaline catalyst(KOH). Finally, some biodiesel properties have been done and compared with pure diesel.

II. **Materials and methods**

A. *Materials*

Egyptian Jojoba oil (green gold): supplied from Egyptian Natural Oil Company. Jojoba is a semi-arid evergreen shrub; this plant is being cultivated in many places in the Egyptian desert. Jojoba seed can yield up to 60% pure oil. It is composed mainly of straight chain monoesters in the range of C26–C48. It is a mixture of long chain esters (97–98 wt. %) of fatty acids and fatty alcohols and therefore is more properly referred to as a wax that gives it a great advantage as natural oil for industrial purposes, which also make it environmentally safe. The technical specifications of Egyptian Jojoba oil are listed in Table. I

- Methanol: Anhydrous methanol (Fluka CO., ASSAY :> 99.8%) most common used due to low cost, availability and its physical and chemical advantages (polar and shortest chain alcohol).
- Anhydrous Na2SO4 (>99%) which is used to water removal from biodiesel produced.
- Potassium hydroxide (KOH) (>85%): It is a base catalyst which is widely used in the transesterification process.

B. *Methods*

B.1. *Transesterification of Egyptian Jojoba oil with KOH catalyst*

TABLE I: TECHENICAL SPECIFICATIONS OF EGYPTIAN JOJOBA OIL SUPPLIED BY EGYPTIAN NATURAL OIL COMPANY

Freezing point	10.6 – 7.0 ° C
Melting points	6.8 – 7.0 ° C
Boiling point	382 ° C
Specific conductivity (27 ° C)	$8.86*10^{-13}$ mho/cm
Specific gravity , 25 ° C / 25 ° C	0.863
Viscosity Cannon – Fenske , 25 ° C Cannon – Fenske , 100 ° C	 50 cP 27 centistokes
Viscosity index	232
Flash point	295 ° C
Iodine value	82 mg KOH/g oil
Average molecular weight	606

In a one liter 3-neck round bottom flask, 100 ml of Egyptian Jojoba oil were heated and stirred in a water bath equipped with magnetic stirrer (Wisdstir, temperature range up to 400 °C & stirring range up to 1700 rpm) to the required temperature (20 - 65 ˚C) at 1000 rpm . KOH in the ratio (0.3 -2 %by weight of oil) was added to methanol (3:1-10:1 molar ratio to oil) in a separate flask and carefully shake till KOH became completely soluble in methanol (methoxide is formed). Methoxide was added to the heated oil. The product was left in a separating funnel for 12 hours and then the ester layer was collected after complete separation by washing with hot water for 5-6 times and using anhydrous Na_2SO_4 for drying. The yield was determined by measuring the volume of ester layer (biodiesel) and the conversion was determined using gas chromatography and quadruple Mass Spectrometers [GC-MS].

B.2. *Analysis*

Gas chromatography and quadruple Mass Spectrometers [GC-MS] from Mesloo Company. (Column :TR5-MS, 30mm*0.25mm, IDX 0.25 µm film, Temperature program: 100 ˚C for 5 min, 5 ˚C/min to 250 ˚C and hold for 10 min ,Carrier gas: helium(He) with flow rate 1 ml/min. Injection temperature: 230 ˚C and Injection Mode: split flow 10 ml/min. Mass spectral library to identify the compounds)

The studied variables were:
Time (0.5-3.5 h),Temperature (20-65 ˚C),Methanol :oil molar ratio (3:1-10:1),Amount of catalyst (0.3-2 % by weight of oil) ,Determination of fuel properties of biodiesel blending with diesel and compared with pure diesel.

III. **Results and discussion**

a. Effect of reaction time

The conversion rate of biodiesel was studied as a function of contact time. "Fig.1'' shows that the conversion rate increases with reaction time .Initially the reaction is slow due to the mixing and dispersion of alcohol into the oil as reported by Freedman et al [29], gradually after that the reaction proceeds faster until maximum yield is reached and then remains constant with any increase in the reaction time .This result is showing good agreement with literature [30-32].

The relation between the reaction time and the true yield of biodiesel produced can be simulated using the following equation:

$$y = 7.638 * t + 64.495 \qquad R^2 = 0.978 \qquad (1)$$

Where y is the true yield in (vol. %) and t is the reaction time in (h).

True yield= yield *conversion

This model is valid for $0.5 \leq t \leq 3.5$

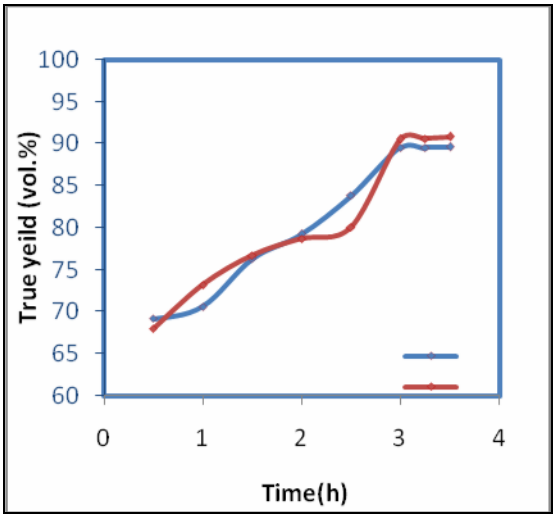


Fig. 1 Effect of reaction time on the true yield of biodiesel at different methanol: oil molar ratio (60 ºC, 0.5% KOH, 1000 rpm)

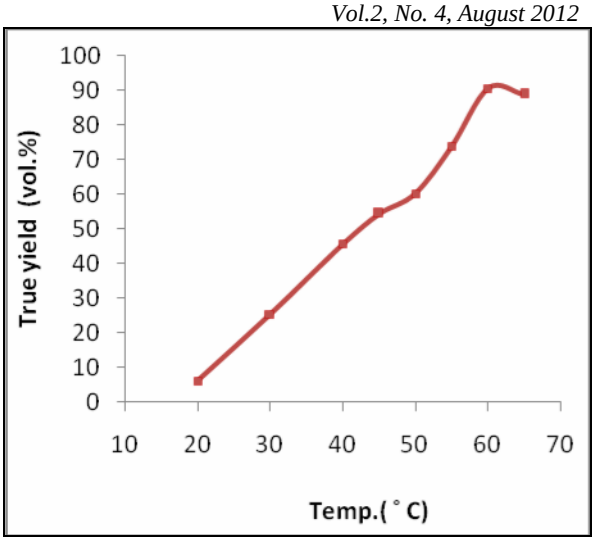


Fig. 2 Effect of temperature on the true yield of biodiesel (1000 rpm, (6:1) methanol: oil molar ratio, 3h, 0.5% KOH)

b. Effect of reaction temperature

Temperature has a strong effect on the reaction and the yield of biodiesel production as shown in "Fig.2''. A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur and as a result the yield of the biodiesel product is improved. However, the reaction temperature must be less than the boiling point of alcohol (boiling point of methanol is at 67 ºC at atmospheric pressure) The maximum true yield is obtained at 60 ºC and after that the yield of biodiesel decreases if the reaction temperature was increased because a higher reaction temperature will accelerate the saponification reaction or evaporation of methanol alcohol which results in a lower yield [33-35].

The relation between the reaction temperature and the true yield of biodiesel produced can be simulated using the following equation:

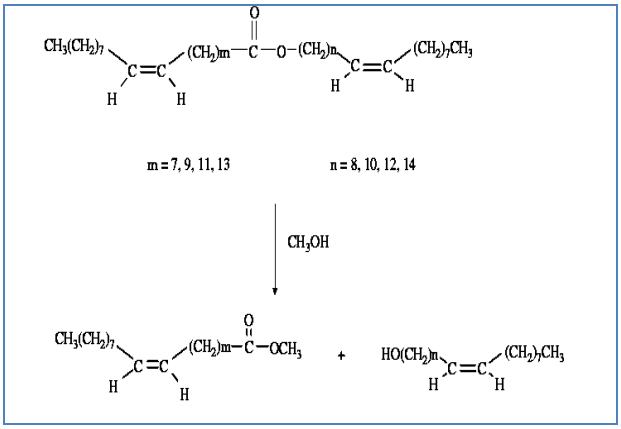
$$y = 1.9324 * T - 32.703 \qquad R^2 = 0.9413 \quad (2)$$

Where y is the true yield in (vol. %) and T is the temperature in (^{o} C).

This model is valid for $20 \leq T \leq 65$

c. Effect of Molar ratio of methanol to oil

Transesterification reaction of jojoba oil wax with methanol takes place according to scheme (1) [36].



Methyl jojoboate jojobal alcohol

Scheme (1). Transesterification reaction of jojoba oil wax with methanol.

The stoichiometric ratio for the transesterification reaction involves 3mol of methanol and 1mol of oil to produce 3 mol of fatty acid ester and 1mol of jojobate alcohol. Excess methanol is used during transesterification to ensure that the oils will be completely converted to ester according to the forward reaction. Furthermore, a higher alcohol ratio can result in a greater ester conversion in a short time [36]. The reaction was carried out at 60 ± 1 ºC with stirring at 1000 rpm and 0.5 wt% of KOH as catalyst. The molar ratio of methanol to oil was varied

between 3:1 and 10:1. "Fig.3'' shows that the molar ratio of methanol to oil (6:1) gives the maximum true yield (90.5) beyond this ratio, further methanol addition has no effect on ester formation; rather it raised process cost. This result show good agreement with previous studies [37-39].

The relation between the methanol: oil ratio and the true yield of biodiesel produced can be simulated using the following equation:

$$y = -1.566 * J^2 + 25.756 * J - 13.538$$
$$R^2 = 0.857 \qquad (3)$$

Where y is the true yield in (vol. %) and J is the Methanol: oil molar ratio.

This model is valid for $(3:1) \leq J \leq (10:1)$

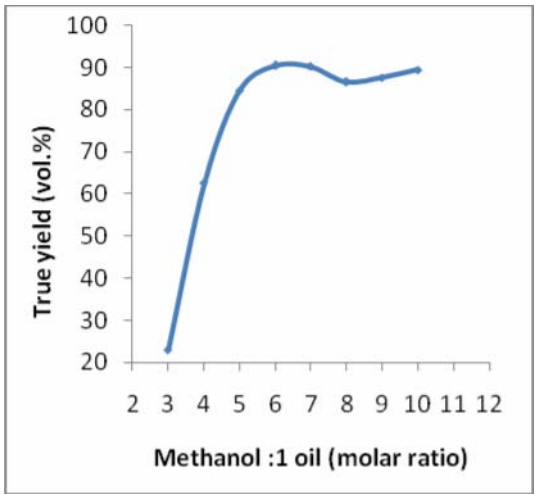


Fig.3 Effect of methanol: oil molar ratio on the true yield of biodiesel (60˚C, 1000 rpm, 0.5% KOH, 3h)

d. Effect of catalyst percentage (KOH) by weight of oil

The transesterification of jojoba oil wax with methanol can be carried out by two alternative methods; acid catalyst and base catalyst. The catalyst concentration can affect the yield of the biodiesel produced. Basic catalysts are usually preferred to acid catalysts because of the higher reactivity and the lower process temperature required [40].Potassium hydroxide is a base catalyst which is widely used in the transesterification process.

The performance of KOH was better than that of NaOH as reported in the previous studies [41]. The reaction was carried out at 60 ± 1 ºC with stirring at 1000rpm and 6M methanol to oil. The wt % of KOH was varied from 0.3 to 2.
"Fig.4'' shows that maximum true yield of biodiesel (90.5) has been achieved at 0.5 wt% of KOH and the true yield decreases as wt% of KOH increases beyond 0.5 wt % due to soap formation [33].

The relation between the wt % catalyst and the true yield of biodiesel produced can be simulated using the following equation:

$$y = -48.24 * W + 116.9 * W \qquad R^2 = 0.98 \qquad (4)$$

Where y is the true yield in (vol. %) and W is the wt% catalyst.

This model is valid for $0.3 \leq W \leq 2$

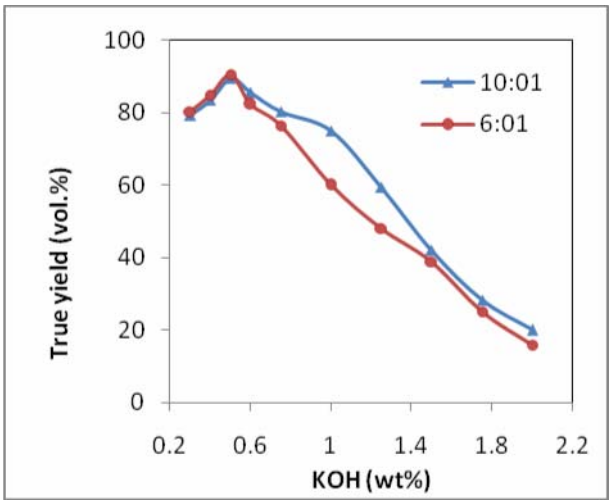


Fig.4 Effect of catalyst (wt% of oil) on the true yield of biodiesel (different methanol: oil molar ratio, 60 ºC, and 3h, 1000 rpm)

Effect of operating variables on the production of biodiesel yield lead to the following numerical overall correlation using regression analysis:

$$\mathbf{y = 2.58 * t + 1.33 * J + 1.406 * T - 41.903 * W}$$
$$R^2 = 0.978 \qquad (5)$$

This equation can be used to predict the true yield of biodiesel in terms of the operating conditions (reaction time, methanol: oil molar ratio, temperature and catalyst wt %). "Fig. 5'' shows the comparison

between the predicted true yield and experimental true yield.

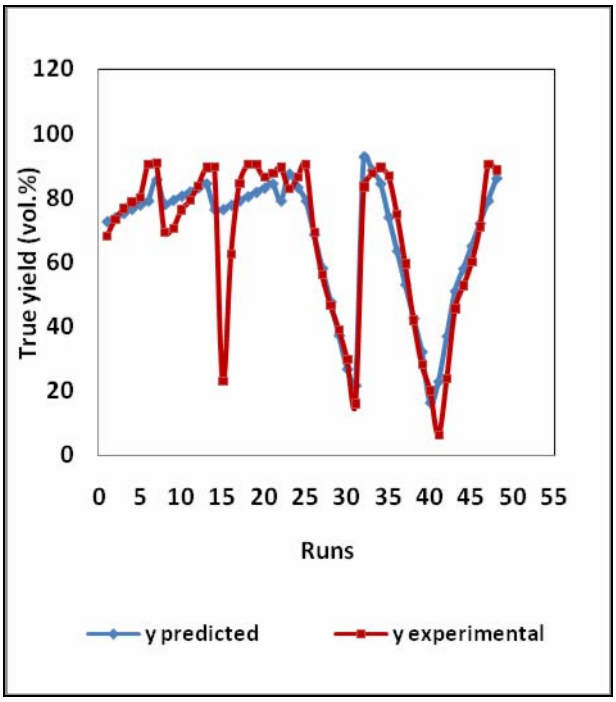


Fig.5 Comparison between the predicted true yield and experimental true yield

e. Biodiesel properties

The high viscosity of biodiesel from plant origin oil is due to large molecular mass and chemical structure leads to problems in pumping, combustion and atomization in the injection system of diesel engine. To solve the problems associated with high viscosity, the following usual methods are adopted: (1) Blending in small blend ratios with pure diesel fuel, (2) micro-emulsification with methanol or ethanol, such as preheating the oils, (3) transesterfication and thermal cracking or pyrolysis and conversion into biodiesel fuels.

In this work, blending with pure petro diesel (B10, B20) and pure biodiesel (B100) was tried and determine the physiochemical properties, Where: 100% biodiesel is referred to B100, 20% biodiesel, 80% petro diesel is labeled B20,10% biodiesel, 90% petro diesel is labeled B10 ,100% pure petro diesel is referred to D100

Higher blends, even B100, can be used in many engines with little or no modification. The use of blends of biodiesel and diesel oil is preferred in engine to reduce emissions of unburned hydro-carbons, carbon dioxides, carbon mono oxides and sulfates. The conventional pure petro diesel fuel is supplied by a local petroleum company in Egypt .Pure biodiesel from Egyptian jojoba oil (no additives are used nor did it subject to any further chemical treatment) used was prepared .B10 and B20 have been prepared in the chemical laboratory of local petroleum company in Egypt. Fuel properties of pure petro diesel, B100, B10 and B20 are determined according to standard ASTM and the results given in Table II. The results indicated that good potential for using biodiesel produced from Egyptian jojoba oil as an alternative diesel engine fuel.

TABLE II CHEMICAL AND PHYSICAL PROPERTIES OF BIODIESEL

Property	**Unit**	**ASTM method**	**Petro diesel Used in blending (D100)**	**Biodiesel standard**	**Ref.**	**Egyptian Jojoba oil**	**Egyptian Jojoba biodiesel**		
							B10	**B20**	**B100**
Kinematic viscosity at 40˚C	**(Cst)**	**D-445**	**3.4**	**1.9-6.0**	**[28]**	**24.75**	**3.82**	**4.25**	**8.84**
Kinematic viscosity at 100˚C	**(Cst)**	**D-445**	**1.43**	**--------**	**------**	**6.43**	**1.55**	**1.66**	**1.97**
Viscosity index	**VI**	**D-2270**	**400.1**	**----------**	**------**	**233**	**284.9**	**228.2**	**191.8**
Density at 15˚C	**Kg/L**	**D1298**	**0.841**	**0.86-0.89**	**[28]**	**0.863**	**0.8407**	**0.8417**	**0.8603**
Cetane no.		**D613**	**50.2**	**45-68**	**[28]**	**53.5**	**52**	**52.5**	**53**
Flash point (C.O.C)	**˚C** **K**	**D-93**	**65** **338**	**Min.130**	**[28]**	**295** **568**	**182** **455**	**286** **559**	**198** **471**
Nitrogen content	**(wt/wt)%**	**D-5762**	**0.0084**	**----------**	**------** **--**	**0.0007**	**0.007**	**0.006**	**0.00075~0**
Sulfur content	**(wt/wt)%**	**D-4294**	**0.219**	**0.05**	**[28]**	**0.002**	**0.182**	**0.161**	**0.00019~0**
Ash	**(wt/wt)%**	**D-1119**	**0.008**	**<0.02**	**[28]**	**--------**	**0.0036**	**0.007**	**0.003**
Water content	**(wt/wt)%**	**D-95**	**0.4**	**0.05**	**[28]**	**---------**	**0.1**	**0.15**	**0.05**
Calorific value	**MJ/Kg**	**D-4868**	**44.3**	**38-43**	**[28]**	**----------**	**45.56**	**45.5**	**45.5**

IV. Conclusion

This study revealed that biodiesel produced from Egyptian jojoba oil can be used as an alternative fuel in conventional diesel engines. The results showed that the production of biodiesel from Egyptian jojoba oil by transesterification with methanol in presence of an alkaline catalyst (KOH) is affected by reaction time, methanol: oil molar ratio, catalyst concentration and temperature. The best yield percentage was obtained using a methanol: oil molar ratio of 6:1, KOH as catalyst (0.5%) and 60 ± 1 ºC temperature for 3 h at 1000 rpm. The yield of biodiesel was determined according to GC-MS. From the results it was clear that the non-edible oil (Egyptian jojoba oil) can be used as a source for production of biodiesel fuel. Numerical correlation using regression analysis for the yield of biodiesel produced with the operating conditions of the transesterification process was presented. The correlation equation can be used to predict the yield of biodiesel in terms of the operating conditions within the range studied. Biodiesel produced (B100) has higher flash point and Cetane number than pure petro diesel. The recommended blending is B10 due to its viscosity and some properties better than pure diesel.

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