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Direct Conversion of Dry Algae to Biodiesel under Supercritical Methanolysis

S. Hawash, S. A. AboEl-Enin & G. ElDiwani*
Chemical Engineering & Pilot Plant Dept. National Research Center
*Email: sanaa_enin@yahoo.com

Abstract – **The study demonstrates a one-step process and environmentally friendly approach for the direct conversion of dry algalbiomass to crude biodiesel under supercritical methanol conditions. Methanol is used for the simultaneous extraction and transesterification of lipids in algae to produce fatty acid methyl esters at supercritical conditions. The process conditions prevented the formation of by-products and the fatty acid methyl esters are produced from polar phospholipids, free fatty acids, and triglycerides. The effects of dry algae to methanol (weight/volume) ratio (1:12-1:40),reaction temperature (150-300°C), and reaction time (5–50 min.) on the yield of fatty acid methyl esters are studied. Conversion percentage reached97%at 300°C, molar ratio 1:30(weight/volume) and reaction time 30 minutes. The purity of fatty acid methyl esters is determined using Gas Chromatography analysis to record80%and alkyl ester content about77.6%.This green conversion process has the potential to provide an energy-efficient and economical route for biodiesel production with high efficiency of high predicted cetane number(60), high resistance for oxidation and low viscosity.**

Keywords – **Biodiesel, Microalgae, Oilextraction Supercritical Methanolysis, Transesterification**.

I. INTRODUCTION

Microalgae can significantly contribute to solve the environmental problems of the global warming associated with burning of fossil fuels**.**Microalgae have been considered as one of the most promising feedstocks for biodiesel production due to their short cell cycle (within 24 hrs.). High oil content (20% - 50%), strong adaptive capacity to environment (high salinity, heavy metal ion, toxicants, high CO_2 concentration, etc.) and no occupation for cropping area.The fuels produced from microalgae oils do not compromise the production of food, as it is the case with oil crops [1]. Biodiesel production from microalgae biomass is particularly one of the most promising clean carbon-neutral sources of energy [2].Different technologies are currently available and used in the industrial production of fatty acid methyl ester (FAME) as a biodiesel fuel [3]-[6].Algal biodiesel can be produced from algal biomass through a series of steps including preparation of dry algae powder, extraction of algal oils with chemical solvents [7], and conversion of the algal oil to biodiesel with a catalyst[1]. Drying the biomass and extraction of algal oils by conventional methods are both energy- and cost-intensive. An alternative to the conventional extraction and transesterification methods is the supercritical process. The biodiesel production under supercritical conditions is a catalyst-free chemical reaction between triglycerides and low molecular weight alcohols, such asmethanol and ethanol, at a temperature and pressure over the critical point of the mixture. At supercritical conditions, the reactive mixture is homogenous avoiding the mass transfer limitations present in the alkali process due to the liquid-liquid partial miscibility of alcohols and triglycerides [8]. Thus, the reaction rate increases because of the high temperature and triglycerides can be converted completely toward fatty ester in less than 30 min. Moreover, the purification step is simpler because of the absence of catalyst.

The direct supercritical methanolysis of algal biomass has been proposed recently as an alternative energy efficient technology and economical route for algal biodiesel productionthat, the presence of water did not have a significant effect on the yield [9].Based on these results, the aim of the present study was to investigate the methanolysis of the lipids present in microalgae Spirulina Platensis strain by a single-step supercritical process under different conditions according to previous works [10]-[13], a methanol/algae mass ratio, temperatures and reaction times. The methyl esters obtained have been characterized for their applications as biodiesel in internal combustion engine using Gas Chromatography (GC)analysis.

II. MATERIALS AND METHODS

A. Materials

Microalgae cells of Spirulina platensis were obtained as dry biomass from the Microbiology Department Soils, Water and Environment Res. Inst., ARC, Giza, Egypt. The culture medium used was the same of Zarrouk's medium [14].All chemicals and solvents used were of analytical grade. Methanol (99.9%) used for the supercritical reaction, n-hexane to separate the methyl esters of biodiesel. For determination the percentage of oil in algal cells,different solvents are used, chloroform, iso-propanol, n-hexane and methanol.

B. Lipid percentage determination:

The dry mass of Spirulina platensis were subjected to two methods for oil extraction:

-Modified method of Folch and Bligh & Dyer's,[15]

By mixing chloroform-methanol(1:1,v/v) with the dry cells using homogenizer Model WiseTis HG-150, for 5-minutes at 800 rpm in a proportion of 1g in 20 mL of solvent mixture. The homogenate mixturesubjected to a magnetic stirring at room temperature for2hr. Cell residue was removed by filtering through Whatman GF/C paper. The filtrate was washed with 0.2 volumes (4 mL for20 mL distilled water). After overtaxing, for few seconds, themixture was transferred into a separating funnel. After settling, the solvent mixture was partitioned into two distinct phases: a bottom dark-green chloroform layer

containing most of the extracted lipids and a top light green aqueous methanol layer containing most of the co-extracted non-lipid contaminants. The chloroformis evaporated in a rotary evaporator and the weightof the crude lipid obtained from the sample isevaluated.

-Hexane-isopropanol extraction method, [16]

A mixture of n-hexane and isopropanol (3: 2, 300 ml) wasadded to 4g of algal powder. The mixture was agitated at 800 rpmfor 5-minutes using homogenizer Model WiseTis HG-150and then, subjected to a magnetic stirring at ambient conditions for 2hrs. Cell residue was removedby filtering through Whatman GF/C paper. The filtrate wastransferred into a separating funnel and sufficient hexaneand water (approximately 40 mL each) were added to inducebiphasic layering. After settling, the solvent mixturewas partitioned into two distinct phases: a top dark-greenhexane layer containing most of the extracted lipids anda bottom light green aqueous-isopropanol layer containingmost of the co-extracted non-lipid contaminants. Thehexaneevaporated using a rotary evaporator to enable gravimetricquantification of the lipid extract. The crude lipidwas re-dissolved in hexane (approximately 20 mL) andtransferred into a sealed glass vial for storage.

C. Experimental set- up and procedure:

The supercritical methanolysis were carried out in a stainless steel batch reactor of 500 ml capacity, assembled with a thermocouple thermometer (± 1.5 K) and a pressure gauge (±2.5 bar). The non-catalytic supercritical methanol transesterification is performed at 250°C.

The experimental protocol for one-step supercritical methanolprocess is as follows:10g of dry algae was subjected to a non-catalytic supercritical methanol (SCM) process in a 500 mL PARR reactor under a matrix of conditions: reaction times of 5,10, 20,30 40 and 50 min; reaction temperatures of 150, 200, 250,and 300^{o}C,and dry algae to methanol weight/volume(wt./vol.) ratios of 1:12, 1:20,1:30 and 1:40, The volume of reaction mixture was from 240 ml to300ml. The pressure inside the reactor varied according to the process temperature. After the reaction was completed, the reactor was subjected to sudden cooling. The reaction mixture was collected and filtrated to separate the algal cells.

The filtrate was transferred into a round-bottom flask and freed from excessmethanol and volatiles at a reduced pressure in a rotary evaporator. The remaining products were transferred into a separating funnel after adding a non-polar solvent (e.g. hexane) for methyl ester separation. The separation led to the upper organic layer containing non-polar lipid and the glycerol settledin the bottom phase. Neutral components were eluted with the solvent,freed from the solvent by its evaporation and drying the product at 65 ºC, till constant weight.

D. Analysis for product characterization and yield calculation:

The fatty acid profile of the extracted oil sample of Spirulina sp. was determined by converting the fatty acids in the oil to fatty acid methyl esters (FAMEs). The FAME composition was determined using a Gas-Chromatography (GC) with a split automatic injector and silica capillary column DB-5 (length: 60 m; ID: 0.32mm. Helium was used as carrier gas at a flow rate of 1 mL/min. The column was held at 150ºC for 1 min and ramped to 240 ºC, at rate 30 ºC/min, and it was then held at 240ºC, for30min. Standards were used to give rise to well-individualized peaks that allow the identification of the fatty acids composition.

In order to determine the reaction yield form, a single run was cooled to 55°C, filtrated and transferred to a separating funnel. Separated layer of biodiesel (ester and unreacted triglyceride) and glycerol were visible yet after 15 min, however full separation was achieved after 16 h. The yield calculated according to following formula:

$$Yield\ \% = \frac{Mass\ of\ ester\ layer\ after\ separation}{Total\ mass\ of\ reactants\ at\ reaction\ start} \times Purity\% \quad (1)$$

Where, purity is fraction of esters in the biodiesel layer obtained by GC analysis according to the method SRPS EN 14103. The conditions of GC analysis were as mentioned above. A standard mixture of methyl esters was used for qualitative analysis and methyl heptadecanoate (above 99%, Fluka) was used as the internal standard for quantification purposes [17].

The percentage of purity of obtained biodiesel under the optimum supercritical conditions was also determined where; the fatty acid methyl ester content in the final product was calculated by taking the ratio of total peak areas of FAME to peak area of the internal standard.

Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. Some equations correlate cetane number with the composition of biodiesel. In this case, it was necessary to use literature data for the fatty acids composition of the fuel used in testing the property equation [18]. In this work, the correlation formulated by Clements[19] was used obtaining a good correlation between reported and predicted biodiesel cetane numbers using the following equation(2):

$$CN = \sum X_{ME}\ (wt.\ \%).CN_{ME} \quad (2)$$

Where CN, is the cetane number of the biodiesel.
X_{ME}, is the weight percentage of each methyl ester.
CN_{ME}, is cetane number of individual methyl ester.

III. Results and Discussions

A. Total lipid content

The highest lipid percentage 9%was obtained by Folch and Bligh & Dyer's method. Hexane-isopropanol extraction method was revealed 8%of oil content present in the dry cells of Spirulina platensis microalgae species. The analysis of algal oil as fatty acid methyl esters (FAME) were determined by gas chromatograph (GC), as shown in Table (1). The most abundant saturated fatty acid were Palmitic acid (C16:0), and Stearic acid (C18:0). The most abundant unsaturated fatty acid were Oleic acid (C18:1) and Linoleic acid (C18:2). In a previous research [20], Palmitic, stearic, oleic and linoleic acids were recognized as the most common fatty acids contained in biodiesel. In particular, oils with oleic acid content have been reported to have a reasonable balance of fuel properties [21].

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Table I: Fatty acids composition of oil content in Spirulina platensis species

Fatty Acids	% of Mass Fraction
C12:0 Lauric acid	1.6
C14:0 Myristic acid	1.6
C16:0 Palmitic acid	61.2
C16-1 Palmitoleic acid	2
C18:0 Stearic acid	7.1
C18-1 Oleicacid	15.2
C18-2 Linoleic acid	5.2
C**20:0** Arachidic acid	6.1
Saturated FA	77.6
Un-Saturated FA	22.4

B. Influence of reaction time

Time of reaction plays an important role in the process economy and productivity. Conventional transesterification reactions take hours to complete while supercritical alcohol transesterification can be achieved in much shorter time periods. For this batch of experiments, the reaction was set at temperature 250°C at which the pressure recorded 125 bars, where the critical temperature of methanol is 240°C and the critical pressure is 79.5bars [27]. Introducing excess of methanol can improve and shift the reaction to right–hand side. So, the effect of reaction time intervals from 5min.to50 min. was set at molar ratio 1:30(wt.: vol.) algae to methanol .As shown in Figure (1), the conversion rate increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After that, the reaction proceeds very fast and the maximum yield reached at reaction time 30minutes (72%).This result is in agreement with Montero et.al, [22], where the biodiesel yields obtained in the direct transesterification of N. oleoabundans increased with the reaction time working at 250°C to attain an 8 wt. % of fatty esters on a dry biomass basis after 30 minutes. The experiments were carried out to determine how excess reaction time affects the yield. As reported elsewhere[23], the fatty acid methyl esters yield decreased at a reaction time longer than the optimum at temperatures above 300 °C due to the decomposition of fatty acid methyl esters. In our study, however, the reaction temperature was held at 250 °C, extending the reaction time reduced the yield.

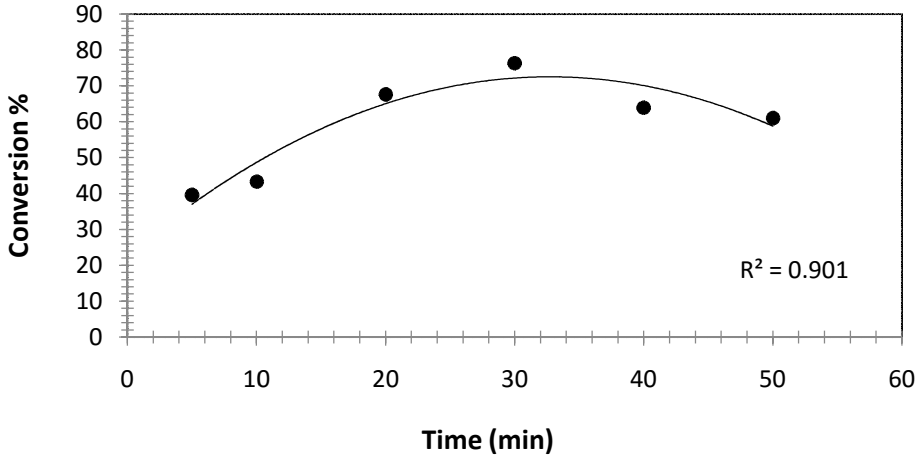

Fig.1. Inflluence of reaction time on the rate of conversion to fatty acid methyl ester at 250°C, 1:30 (wt./vol.) ratio

C. Influence of algae to methanol ratio weight to volume (wt. /vol.)

In non-catalytic supercritical alcohol processes, high algae to methanol ratios are essential to increase the reaction rate and shift the equilibrium towards the methyl esters product side [24], [25]. In this case, methanol acts as a solvent, catalyst and reactant for the extractive – conversion process. To investigate the effect of algae to methanol (wt. /vol.) ratio on biodiesel yield percentage, the ratio was studied from 1:12 to 1:40 while reaction temperature and time were kept constant at 250°C and 30 min. respectively.

As shown in Figure (2), the algae to methanol ratio have a positive effect on the FAME yield up to 1:30, but at higher ratio have a negative impact. This phenomenon was also observed previously when producing fatty acid methyl and ethyl esters from palm oil [26] and wet alga [24], [27] because of the higher ratio ofbiomass to methanol could shift transesterification reaction forward the reversible reaction.

The decrease in yield can be attributed to inhibition caused by the excessive amounts of alcohol present in the reaction mixture at high temperatures [28],[29]. In addition, the higher ratiocontributes to lower the critical temperature of the reaction mixture and cause a reduction in the yield due to the decomposition of FAME. When the reaction mixture is heated above the critical temperature, auto-oxidation of the intermediates organic substrates and/or unsaturated fatty acids is possible during biodiesel production process, leading to the formation of hydro - peroxides that are thermally instable. It was also observed that excess methanol interfere with the glycerin separation due to increase the solubility, which resulted in lower biodiesel yields [30],[31].

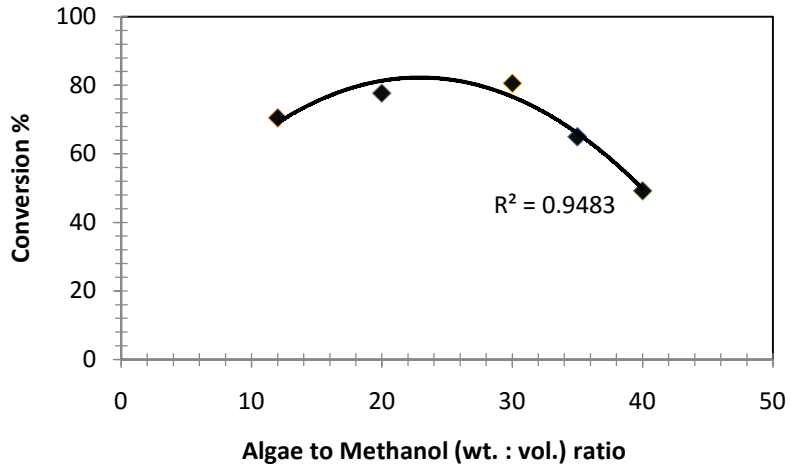

Fig.2. Infllunce of Biomass to Alcohol (weight / volum) ratio on rate of conversion at 250°C for 30 minutes

D. Influence of reaction temperature:

Temperature is a vital parameter in supercritical alcohol transesterification reactions. For the temperature effect runs between 150°C and 300°C, the dry algae to methanol (wt./vol.) ratio was kept constant at 1:12 and reaction time 30min. It should be noted that the critical temperature of the methanol is 240>C, therefore, the reactions at 150°C and 200°C, were done under subcritical state of methanol. As shown in Figure (3), the yield percentage was very low and decrease by increasing temperature from 150 to200°C.This result is in agreement with the previous studies[32],at subcritical state of alcohol the reaction rate is very low .By increasing temperature to 250 and 300°C,the reaction will be done under supercritical conditions and an increase in temperature favored the yield of fatty acid methyl ester with steadily increasing up to300°C[33].When compared to previous work [27], of using ethanol and wet biomass of algae, the yield increased up to265°C and then fell at270°C.The decrease in yield at this temperature can be attributed to the thermal degradation of unsaturated fatty acids present in the algal oil. Similar observation had been reported in other studies[24], for wet algae with methanol. In this work as well, the yield increased up to300°C due to the low percentage of unsaturated fatty acids in the algal oilwhich higher the oxidation stability of biodiesel[20] .

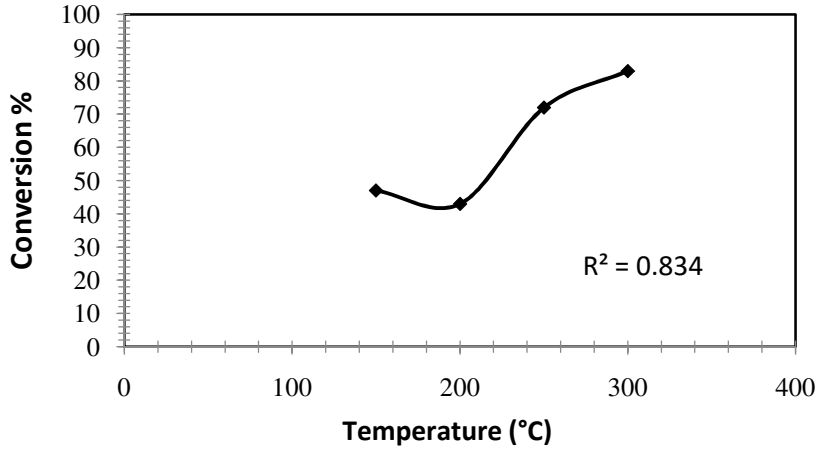

Fig.3. Infllunce of reaction temperature on conversion rate at 1:12 ratio of algae : methanol for 30 minutes

E. The optimum operating conditions:

The experimental results detected the optimum operating conditions which recorded the higher yield of FAME. An experiment was carried out at these optimum conditions,[30min., ratio (1:30) algae to methanol and reaction temperature 300°C], to give yield percentage of 97%. Comparing with previous studies[24],the optimum reaction conditions were varied slightly,[255°C,25min. and wet algae to methanol ratio 1:9],but lower yield of fatty acid methyl esters (FAME) was observed (≤85%), the water–methanol mixture has both strong hydrophilic and hydrophobic properties that help speeding up the reaction

significantly[9],[24]. From another pervious study it was shown that, using ethyl alcohol for wet algae biomass[27], the optimum conditions were varied [265°C,20min.and1:9 (wt./vol.)ratio], but lower yields of fatty acid ethyl esters (FAEE) was observed (67%). The difference in the yield of biodiesel is due to lower reactivity of triglycerides with ethanol than methanol [34], and this was explained as the hindrance of the (–OH) group on the long-chain alkyl group in the alcohol to react with triglycerides to form fatty acid alkyl esters [28].

F. Analysis of fatty acid methyl ester:

The FAME obtained in the direct methanolysis experiments has a dark-brown color. The GC-analysis showed that the purity percentage of obtaining biodiesel under the optimum supercritical conditions was 80%. The content of the fatty acid methyl ester in the final product was calculated according to equation (1) to equal 77.6%. It is noted from GC results that algal biodiesel contains a major proportion of saturated and mono unsaturated fatty acid methyl esters. The major fatty acids methyl ester were palmitic acid ($C_{16\text{-}0}$,33.1-51.3%),stearic acid ($C_{18\text{-}0}$,10.7-17.5%),oleic acid($C_{18\text{-}1}$,10.7-17.6%),linoleic acid($C_{18\text{-}2}$,5.1-9.2%),palmetoleic acid ($C_{16\text{-}1}$1.1-1.5%)and arachidic acid($C_{20\text{-}0}$,0.5-0.3%). The low percentage of methyl ester with carbon chain ≥ 18 prove a low viscosity of the biodiesel [35].The high percentage of palmitic acid methyl ester which is not liable to degradation, considering its high stability [35], [36]. The predicted Cetane number (CN) of biodiesel obtained under the optimum supercritical conditions according to equation (2) was equal 60. Higher the cetane number is better in its ignition properties [37],[38].High cetane numbers were observed for esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids[39]. In this study the algal biodiesel is rich in these compounds.

IV. Conclusion

The direct supercritical methanolysis of algal biomass has been recently as an alternative energy efficient technology and economical route for biodiesel production, in view of:

- It is a catalytic-free chemical reaction.
- Eliminating the oil extraction step through simultaneous extraction and conversion of dry algae biomass to crude biodiesel.

The supercritical methanolysis reaction rate is high because of the high temperature and triglycerides can be converted completely into fatty ester in shorter time (30min.) than the conventional transesterificationreaction. Moreover, the purification step is simpler because of the absence of catalyst. These advantages compensate for the higher capital cost associated to the process.Under supercritical methanol conditions the fatty acid methyl esters can be produced from triglycerides, free fatty acids and polar phospholipids.

The optimal conditions, defined as yielding the highest extent of reaction as 97% conversion with 80% purity which means alkyl ester content 77.6%, was at 300°C, algae biomass to methanol ratio 1:30 and reaction time of 30 minutes. Microalgae of Spirulina platens is species is a promising strain for biodiesel production under supercritical methanol conditions with high performance of low viscosity, high oxidation stability and high predicted cetane number.

Recommendation

Scaling up of process design, reaction kinetics and thermodynamics, optimization and fuel analysis of biodiesel are to be investigated for accurateevaluation of the techno-economic study.

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AUTHOR'S PROFILE

Salwa Ismail Hawash

Was born in Egypt at 8th January 1950, She received her B. Sc. (1973) and Ph. D. (1984), in Chemical Engineering from chemical Engineering Department., Faculty of Engineering, Cairo University. She was a Professor Researcher of Chemical Engineering since 1994 at Chemical Engineering and Pilot Plant Department in National Research Centre, Dokki, Cairo, Egypt,. She is participated in Projects and Preparation of Research Studies Relevant to: Industrial wastewater treatment activities include process description, housekeeping wastewater minimization and proposed treatment options for waste effluents, Chemical Engineering Reactions, Pilot Plant Design and Operation, Water Pollution and Environmental Protection and Development of Biodiesel production.

Sanaa Abd El-Halim Abo El-Enin

was born in 13th September 1956 Cairo, Egypt , She received her B. Sc. (1987), in chemistry (1978), Chemistry Department, Cairo University and her *Ph. D.* in Electrochemistry (1996), Chemistry Deptt. Faculty of Science, Ain-Shams University. She was an associated professor at Chemical Engineering since (1997) at Chemical Engineering and Pilot Plant Department in National Research Centre, Cairo, Egypt. She is interesting in Physical Chemistry, Electrochemistry, Chemical Analysis and Applied Chemistry, Corrosion Protection, Metal Surface Treatment, Environmental Protection and Development in Biodiesel production

Guzine Ibrahim El Diwani

was born in 14 March1947 Cairo, Egypt, She received B.Sc. in Chemical Engineering (1970) Faculty of Engineering, Alexandria University, Chemical Engineering Department and her Ph.D. (1975) in Chemical Engineering (1975), Czechoslovakian Academy of Science, Prague, Tcheck Republic. She is interesting in Chemical Engineering Reactions and Mathematical Modelling, Environmental Engineering Pilot Plant Design and Operation, Process Development and Technology Transfer, Development of New and Conventional Chemical Production, Techno-economic evaluation studies and Biodiesel studies.