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(Research Article)

Sunlight-driven photocatalytic production of biodiesel from palm oil utilizing a solid catalyst composed of a blend of CaO and ZnO

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Abstract

Biodiesel, a promising eco-friendly substitute for petro-diesel, can be efficiently derived from abundant vegetable oils. Among these, palm oil stands out as a prime choice. A transesterification reaction was conducted on palm oil triglycerides with methanol catalyzed by CaO/ZnO blend. CaO serves as strong basic sites which are necessity for activation of methanol as well as triglycerides, whereas ZnO, a type of semiconductor, can absorb sunlight to form electron-hole pairs, thus the photocatalytic efficiency is greatly improved. This effect may reduce the activation energy and hence speeding up the reaction rate. While conventional methods utilize caustic alkalis as catalysts for oil trans-esterification, issues such as unwanted soap formation and reduced biodiesel yield arise with homogeneous alkaline catalysts. This study represents into an innovative approach using a heterogeneous catalyst mixture of CaO and ZnO activated under sunlight to produce biodiesel from waste palm oil and methanol. The study shows that 94% yield of FAME from waste palm oil used as cooking oil using various concentration of catalyst mixture which is sunlight driven. The effect of light, temperature and molar ratio on yield of biodiesel has also been studied in this present study. According to the results of the study, the highest yield of Biodiesel was obtained at 0.5 % catalysts concentration under sunlight at a 1:5 molar ratio. The optimum temperature for obtaining highest yield that has observed is 60˚C. In addition to , it has also been observed that increased concentration of catalysts and lower molar ratio minimized the overall yield of the transesterification.

Keywords: Palm olein; Methanol; ZnO; Photo catalysis; Biodiesel; Transesterification**.**

1. Introduction

Fossil fuel resources are non-renewable and limited, and their applications trigger environmental issues like acid rain, global warming and greenhouse gas pollution [1],[2]. Larger part of energy consumed is based on fossil fuel resources that are non-renewable. The reliance of mankind totally on the conventional fuels could cause considerable deficiency in future [3]. Biodiesel seems to have the ideal physicochemical features and is comparable to traditional petrol-diesel [4]. Biodiesel offers numerous benefits over traditional petroleum diesel. With a higher cetane number, absence of aromatics, minimal sulfur, and 10-12% oxygen content, biodiesel outperforms in reducing CO, HC, and particulate emissions in comparison to petroleum diesel. Biodiesel production from WCO consists of a number of steps like WCO collection, pre-treatment of WCO, viscosity reduction (biodiesel production), and post-production processing [7]. Different methods are available to produce biodiesel, like transesterification, thermal cracking (pyrolysis), micro-emulsification, and dilution The production of fatty acid methyl esters (FAMEs) through transesterification of triglycerides with methanol, facilitated by basic homogeneous catalysts like sodium hydroxides or alkoxides, is a common industrial practice [5]. The goal is to streamline the process, minimizing time, chemical, and energy inputs [6].

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Addressing these issues, a number of studies have been conducted on biodiesel processes, such as acid-catalyzed process, supercritical process of enzymatic process and heterogeneous catalyst process [8],[9]. In particular, the heterogeneous catalyst process is expected to be an effective biodiesel production process with low cost and minimal environmental impact because of the possibility of simplifying the production and purification processes under mild conditions [10]. Therefore, many heterogeneous catalysts for the transesterification of oils have been developed. For example, the transesterification reaction of soybean oil with ETS-10 zeolite has been studied; conversion in excess of 90% was achieved at a temperature of 100°C [11].

2. Materials and Methods

2.1. Materials

Some raw materials are required for the production of biodiesel such as refined palm olein, methanol, ZnO catalyst, CaO catalyst. The reagents like methanol (Acetone Free), Nano Zinc Oxide catalyst (Nano powder≤100nm) was from Sigma-Aldrich,USA. and CaO catalyst (assay≥90%.M.W- 56.07g/mol) was obtained from E. MERCK. The refined palm olein was bought from the Budge Budge Refineries Ltd., Kolkata, West Bengal.

2.2. Methods

2.2.1. Biodiesel Production from Waste Palm Oil

A sequence of experiments was conducted with palm oil under diverse experimental conditions as stated [12]. The effects of sunlight on the concentration and reaction time of ZnO/CaO catalyst mixture were observed in transesterification processes that were heated in a regular mantle heating process. The concentration of ZnO/CaO catalyst (0.05, 0.1, 0.5, 0.75 and 1.0 % (w/w)) and the molar ratios such as 1:3, 1:4 and 1:5 are the operating factors. The reactor was first filled with palm oil, and then methanol and ZnO/CaO were added. The heating operation was conducted at a temperature of 60-65ºC, and a 30-minute reaction time was chosen to begin the reaction. The procedure was repeated for reactions lasting 1.0, 2.0 and 3.0 hrs. The result was left in a separator funnel overnight to separate the methyl ester and glycerol after the reaction was finished. First, three rounds of warm water washing were performed on the methyl ester. The product was lastly dried for one hour at 60ºC.

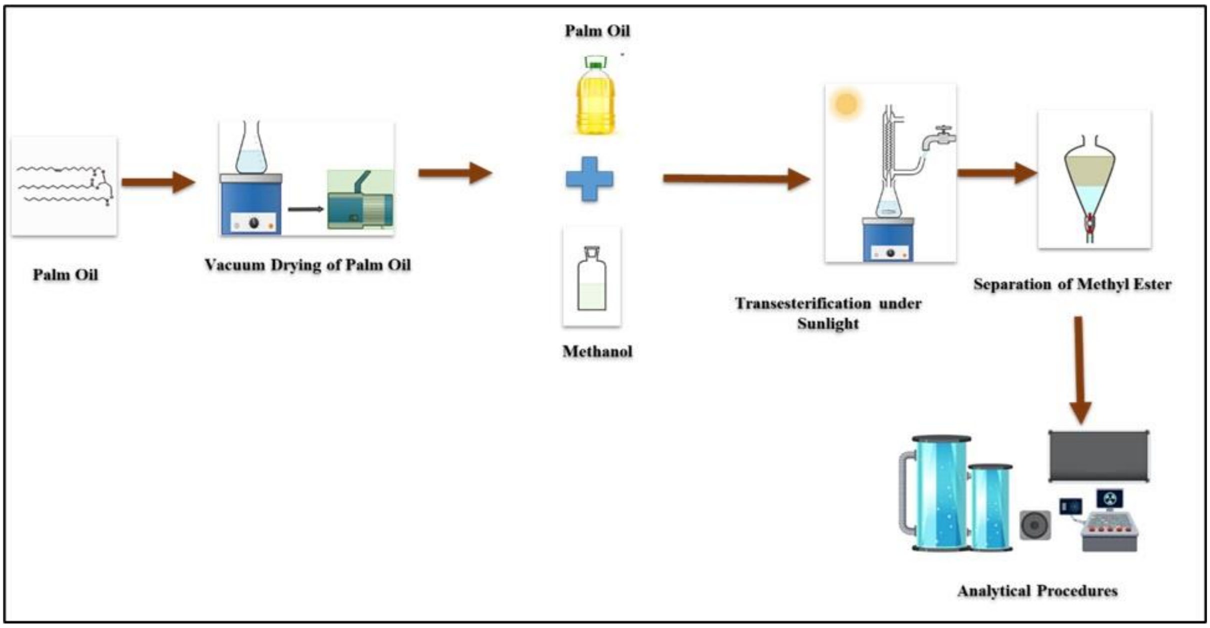

Figure 1 Experimental Setup for Transesterification Reaction

2.2.2. Identifying the Presence of Methyl Ester through TLC:

TLC method was adopted to conduct the qualitative analysis as mentioned by prior studies [13]. The solvent system used for TLC comprised of diethyl ether, hexane and acetic acid at a ratio of 20:80:1 (v/v/v) respectively.

2.2.3. Analysis of Biodiesel

Analyses were carried out for biodiesel concentration on an Agilent 6890 GC with an Agilent 19095N-123 INNOWAX capillary column (30 m × 0.53 mm × 1 µl) and a flame ionization detector. Helium was used as the carrier gas [14]. The biodiesel yield was determined from the percentage of methyl ester content according to the following equation:

Yield (%) = $\frac{w_1 - C_1}{w_2}$

Where. W_1= Actual weight of methyl ester obtained from transesterification (g)

C_1= Amount of methyl ester as measured by GC

W_2 = Total weight of Palm oil used for reaction process

3. Result and Discussion

3.1. Effect of Catalyst Dosage

A transesterification reaction was carried out using 0.05, 0.1, 0.5, 0.75 and 1.0 % (w/w) of CaO catalyst. The impact of catalyst concentration on methyl ester yield as a function of reaction time is displayed in **Figure**. 2. Even if the increase is less noticeable for catalyst concentrations of 0.05, 0.1, 0.5, 0.75 and 1.0 % (w/w), it is evident that a larger concentration of catalyst utilized leads to a higher yield of methyl esters. Because CaO has a lower basicity than homogeneous catalysts, its catalytic activity is not as high as that of KOH or NaOH catalysts. With a catalyst concentration of 0.5% (w/w) and a reaction duration of 1hr, 80.23% is the yield that was produced. Increasing the amount or extending the reaction time will result in a larger yield of methyl esters [15]. It may therefore be concluded that a larger yield of methyl esters is obtained when longer reaction time and a greater catalyst concentration are utilized.

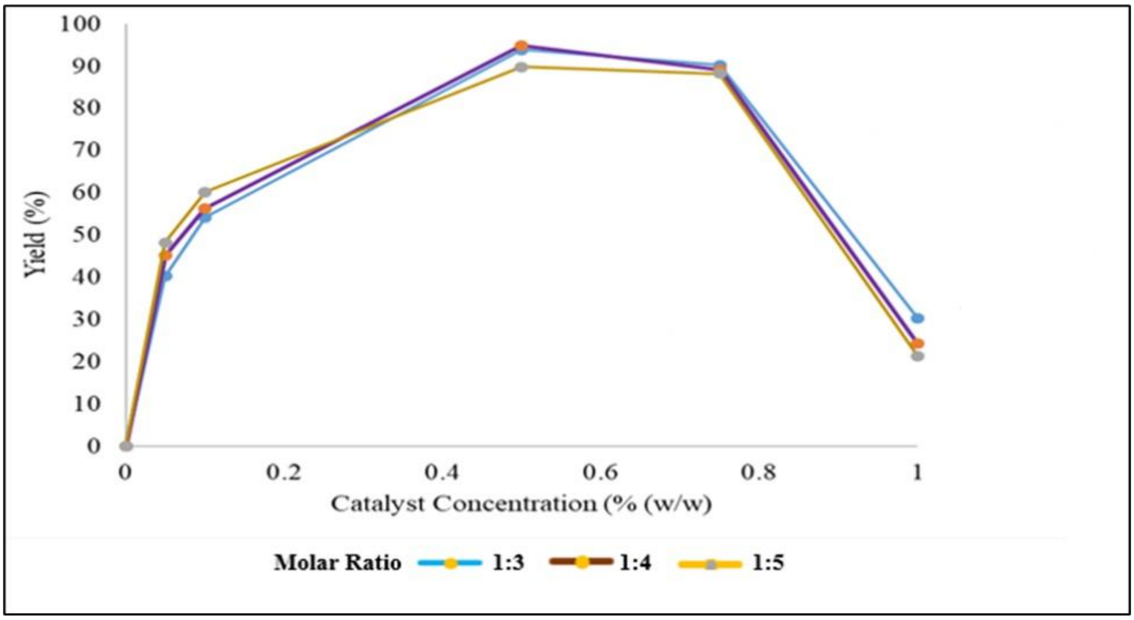

Figure 2 Yield of Methyl ester as a function of catalyst concentration (0.05, 0.1, 0.5, 0.75 and 1.0 % (w/w)

3.2. Effect of Molar Ratio of Methanol to Palm Oil

Palm oil to alcohol ratio impacts on the percentage of fatty-acid methyl ester (FAME) produced. The increase in molar ratio increased the % yield and better yield was observed for methanol at 1:5(oil: alcohol) ratio. It should be noted that the higher amount of methanol limits the transesterification reaction [16]. It is very important to optimize the amount of alcohol for the maximum yield. Thus, the oil ratio to alcohol varied from 1:3 to 1:5. The yield was increased with the increase in oil ratio to methanol, and the maximum yield was obtained at 1:5 oil ratio to methanol. The yield obtained was 94% which is 25.5% more efficient than 1:3 molar ratio of palm oil to methanol as shown in **Figure 3**.

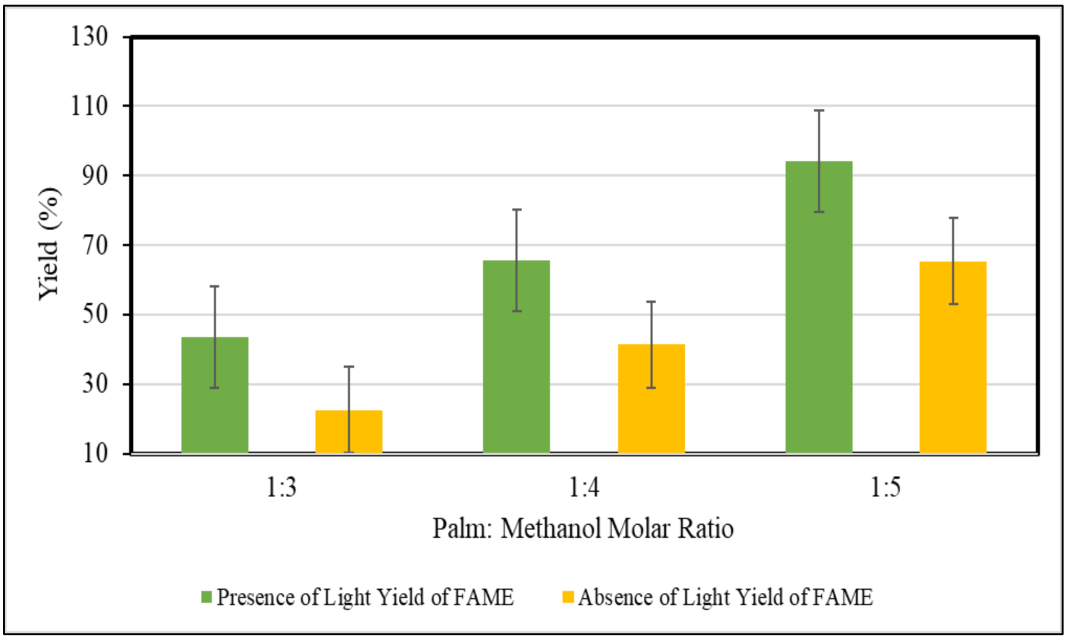

Figure 3 Yield (%) of Methyl Ester as a function of Molar Ratio (Catalyst Concentration 0.5%)

3.3. Effect of Temperature

Temperature variations between 60°C and 80°C were used to investigate the effects of temperature. Temperature was found to be a significant factor in the FAME yield, with a maximum yield of 94% for methanol being reached at 60°C as shown in **Figure** 4. The ester was obtained with mechanical stirring. The Arrhenius equation clearly shows that the increase in temperature increases the rate of reaction. However, the energy requirement increases when high temperature was used [17]. To cut down on operating expenses, it is therefore preferable to run at ambient temperature. Methanol performed better than all the other alcohols that were investigated. At this temperature in presence of photocatalytic (sunlight) the layer was separated.

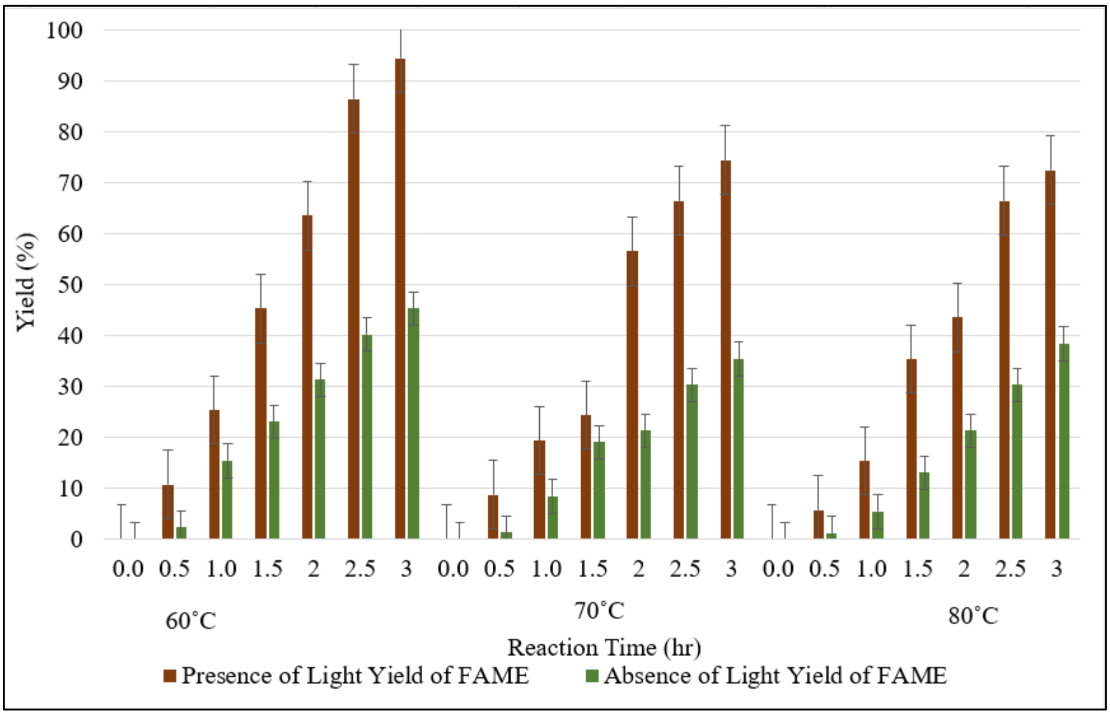

Figure 4 Yield as a function of Reaction Time with respect to different Temperatures (60˚C, 70˚C & 80˚C) at Catalysts Concentration 0.5%

3.4. Effect of Light

The influence of light on the reaction was studied where the whole experiment was conducted without absence of light as well as in presence of light along with different parameters for different sets. As a result, layer separation was found, and the yield of methyl ester was not very good. But when sunlight was provided to the experiment for 3hrs, a layer separation was seen, and the yield of FAME was maximum as depicted in **Figure 5**. It offers the possibility of extending the spectrum of applications to a variety of processes, including oxidations and oxidative cleavages, reductions, isomerizations, substitutions, condensations and polymerizations [18]. The sunlight also helps in direct conversion to methyl ester without forming any intermediate compounds.

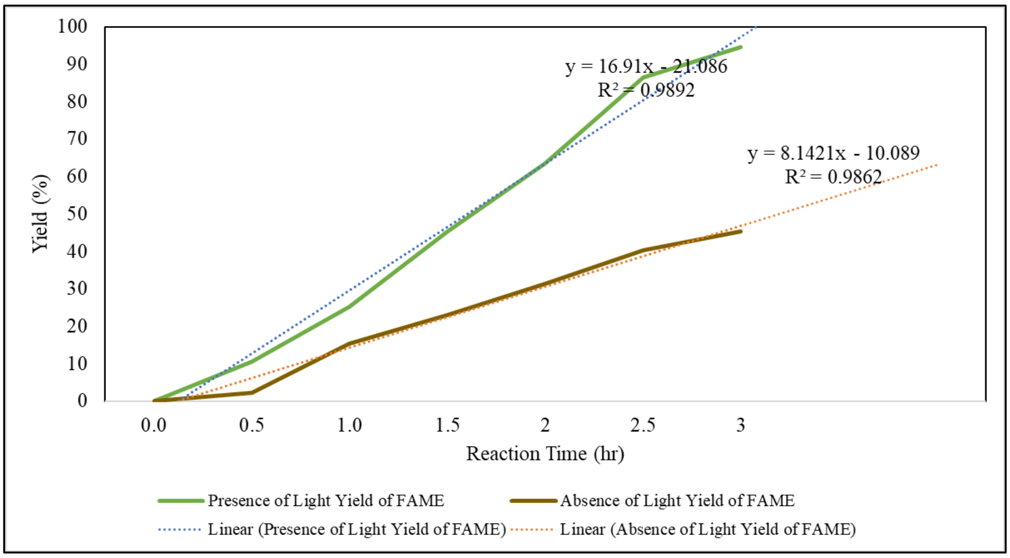

Figure 5 Yield (%) as a function of reaction time at a condition of absence and presence of sunlight at catalyst concentration of 0.5%)

3.5. Effect of reaction time

A study was done on the impact of reaction time. An increase in reaction time resulted in an increase in yield. The yield was 80.23% after 1 hour and 94% after 3 hours, according to the results. In the ideal reaction time was determined to be 3 hours because there is very little yield increase after 1 hour as shown in **Figure 6**. Because there is a higher rate of collision between the reactant molecules during a longer reaction time, more ester is produced than there was during the initial period. The yield has increased two-fold since the beginning. At this particular time in the presence of light the layer was separated.

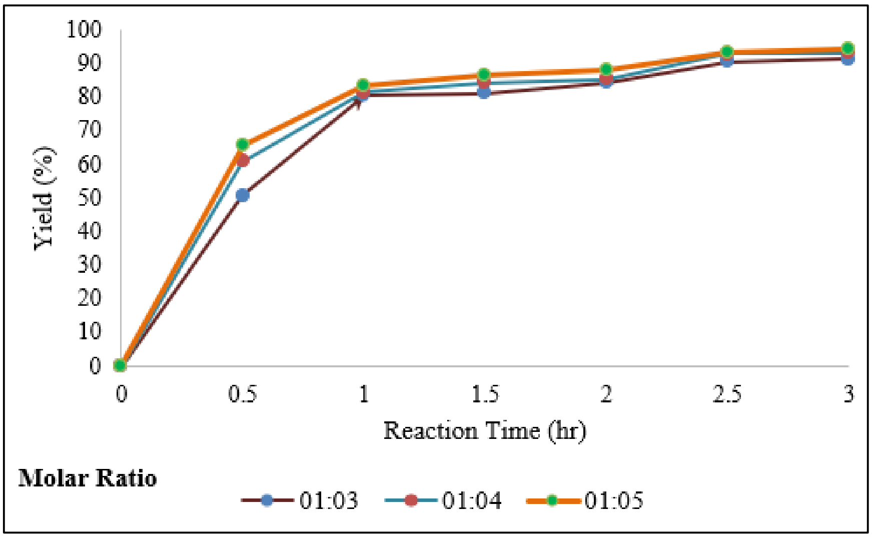

Figure 6 Yield of methyl esters as a function of reaction time (CaO Catalysts of 0.5% (w/w))

3.6. Effect of using ZnO and CaO together as a Catalyst

Zinc oxide can be used as a catalyst since it is stable, re-usable, commercially available and environmentally benign. However, due to its low basicity and catalytic activity, it cannot be used as a support with alkaline metals or blended with other metal oxide to originate a good basic solid catalyst and to improve the catalytic activity for the transesterification of vegetable oils [19]. On the other hand, calcium oxide possesses a high catalytic activity and basic strength. However, it undergoes leaching which influences the quality of the product. Previous studies have demonstrated the use of a combination of CaO with other metal oxides to provide higher yield of FAME [20]. Nowadays, there is an essential need to develop effective and inexpensive catalysts with an environmentally benign process. Thus, in this research a catalyst zinc oxide blended with calcium oxide was designed using co-precipitation method in incubator shaker.

4. Conclusion

Biodiesel is an alternate and renewable energy fuel. Waste Palm oil belongs to the 3rd generation of biodiesel. Approximately 30% of per capita edible oil consumption is generated as waste. The use of Waste Palm Oil reduces the cost of biodiesel production and reduces the load on waste disposal plants. The CaO demonstrated an efficient and effective efficiency as catalyst for the transformation of Waste Palm Oil into biodiesel. Transesterification process was employed for the production of biodiesel. Hence photo catalysis process shows more efficiency. Chemical properties of biodiesel were also determined in comparison to European and American standards, which were in the recommended limit. Based on efficiency, the catalysts are economical which could be used for the conversion of Waste Palm Oil into biodiesel. A thorough analysis of the biodiesel produced is currently underway. The synthesis of nano-particles with sunlight acting as a light source has the potential to make the process environmentally friendly and energy-efficient.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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