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A REVIEW OF THE BIODIESEL SOURCES AND PRODUCTION METHODS

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ABSTRACT

As a result of the rapidly growing population and the developing industry, energy resources are becoming exhausted and therefore it is becoming increasingly necessary to find alternative energy sources. An alternative fuel must be technically feasible, economical, environmentally friendly. One of the alternative fuels is biodiesel. Biodiesel is an alternative, non-toxic, biodegradable and renewable fuel obtained from renewable energy sources. Vegetable oils from oilseed crops such as biodiesel, rapeseed (canola), sunflower, soybean, safflower, animal fats, short chain alcoholic waste in the presence of catalyst can be obtained from home frying oils. Biodiesel does not contain oil; but it can be used as a fuel by mixing it with pure or any oil based diesel. In other words, biodiesel is mono alkyl esters obtained by reaction of vegetable fatty acid esters under certain conditions with simple alcohols such as methanol or ethanol. The types of vegetable oil used as a source of raw materials in biodiesel production are very important. Because the types and ratios of the fatty acids in the oil used indicate the fuel quality of the produced biodiesel. Biodiesel is produced by dilution, microemulsion, pyrolysis and transesterification. In addition, there are studies to treat the wastewater produced during biodiesel production.

In this study, after giving general information about biodiesel and its sources, production methods are discussed in detail. A sample study on the treatment of wastewater generated during the production of biodiesel is also included.

Key Words: Biodiesel, biodiesel production, biomass energy, biodiesel production methods

1.Introduction

1.1.Biodiesel

One of the most important elements of human beings is energy. Petrochemical resources, coal and natural gas make up a large portion of the world's energy needs. As the world's energy needs increase day by day, interest in energy resources has started to increase.

80% of the energy sources used supply of fossil fuels. 70% of fossil fuels are coal, 20% are petroleum and 10% are natural gas [1]. According to the analyses made in line with the utilization rates of the fossil resources, the amount of reservoirs of the existing reserves will decrease substantially in 100 years. Moreover, considering the CO_2 emissions of fossil fuels, environmental pollution is estimated to increase by 50% in the 2030s [2]. In recent years, oil resources have been decreasing and therefore finding alternative energy sources has become an obligation. Among these

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methods, renewable biomass Energy is of great importance. Substances of animal and vegetable origin are classified as biomass energy sources [3].

As an alternative fuel, one of the fuels that are being studied is; It is biodiesel. Biodiesel is an alternative diesel fuel obtained from renewable sources. Biodiesel is produced by reacting vegetable or animal oils with an alcohol and catalyst. It is also a non-toxic, biodegradable and renewable diesel fuel.

Fatty acid alkyl ester derived from oil seed plants such as biodiesel, rapeseed, canola, sunflower, soybean, safflower, animal fats, waste domestic frying oils with a short chain alcohol accompanied by a catalyst is a chemical product of alkyl ester. Biodiesel does not contain oil; but can be used as a fuel, either pure or mixed with diesel oil of any proportion [4]. In other words, biodiesel are mono alkyl esters obtained by reacting vegetable fatty acid esters with simple alcohols such as methanol or ethanol under certain conditions [5].

In this study, after giving general information about biodiesel and its sources, production methods are discussed in detail. In addition, in this study, a study on advanced oxidation methods has been extensively included.

2. Biodiesel Resources

Biodiesel, vegetable and animal oils, recovery oils, municipal and industrial waste origin recovery oils, waste vegetable oils, used frying oils and algae are produced.

Oil sources that can be used in biodiesel production:

- **Vegetable Oils:** Sunflower, Soybean, Rapeseed, Safflower, Cotton, Palm Oils
- **Recovery Oils:** Vegetable Oil Industry By-Products
- **Urban and Industrial Waste Origin Recovery Oils**
- **Animal Oils:** Frost Oils, Fish Oils and Poultry Oils
- **Waste Vegetable Oils:** Used Cooking Oils

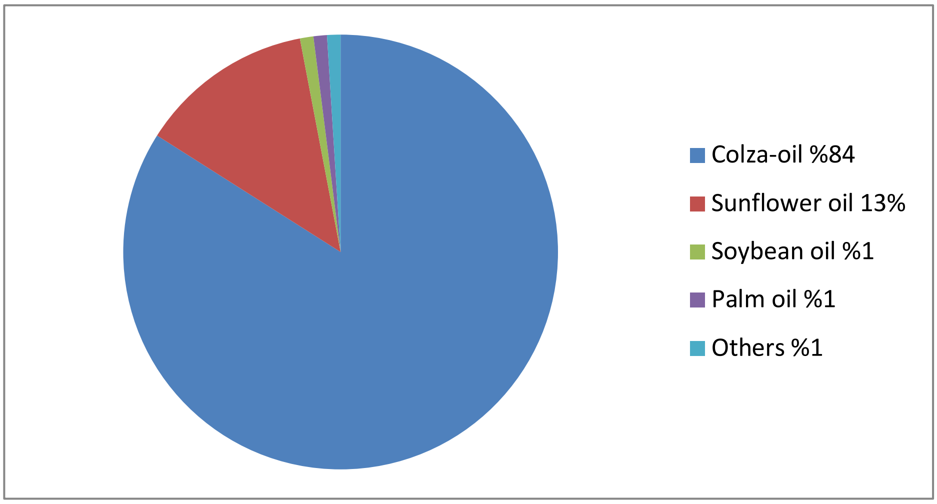

Figure 1. Sources of raw materials used in biodiesel production [6]

Figure 1 shows the distribution of raw material resources used in biodiesel production. Accordingly, rapeseed oil is the most used raw material with 84%, followed by sunflower oil with

13%. Soybean, palm oil and other raw materials have a share of 1% in production. Rapeseed oil (canola oil) is the most important type of vegetable oil used in transesterification and canola oil is very suitable for high quality biodiesel production. Germany and Austria are the leading countries in the production of canola-based biodiesel. Sunflower oil is widely used in biodiesel production in Southern France and Italy, soybean oil in USA, palm oil in Malaysia. The USA, Austria and the UK are the leader countries that produce biodiesel based on used cooking oil. The most important problem in biodiesel production is the regular and continuous supply of raw materials [6].

The type and amount of vegetable oils used as raw material sources in biodiesel production are very important. Because the types and proportions of the fatty acids in the oil used show the fuel quality of the biodiesel produced.

3.Biodiesel Production

3.1.Dilution Process

Dilution process; is a process of thinning vegetable and waste oils by mixing with a solvent or a diesel fuel in certain proportions. The most common of these processes is the mixing of oils with diesel fuel. This reduces oil viscosity and reduces diesel fuel utilization [7]. In the applications, mixing ratios of oils with diesel fuels are expressed as: B20, B30, B40, B50, B80. In short, there are 20%, 30%, 40%, 50% and 80% vegetable, animal or waste oil. Oils used in the dilution method of biodiesel production; peanut oil, rapeseed oil, sunflower oil and waste oils [8].

3.2.Microemulsion Creation Method

Another method used to reduce the high viscosity of vegetable oils is microemulsion with short-chain alcohols such as methanol, ethanol or 1-butanol. Microemulsion is the equilibrium distribution of optically isotropic liquid microstructures with dimensions between 1 and 50 nm, normally formed by a combination of two immiscible liquids and one or more active substances [9].

The short-chain alcohol methyl and ethyl alcohol have the disadvantage that the microemulsified vegetable oil has lower heat values than the petroleum diesel fuel due to the presence of alcohol.

3.3.Pyrolysis Method

Pyrolysis consists of thermal decomposition of oils in the presence of air or nitrogen gas. The fuel obtained by pyrolysis can be made cheaper than that obtained by transesterification. This is possible using low quality raw materials. For example; Pyrolysis can be used as raw material for restaurants' food oil wastes, transesterification process oil wastes and oil products from factories producing food oil [10].

Pyrolysis is firstly decomposed by heat energy in a closed container of vegetable oils. Secondly, the prepared materials are decomposed as thermal energy by distillation and vegetable and waste oils and the obtained biodiesel shows similar properties to diesel fuels.

In this method, vegetable oil molecules are broken down into smaller molecules in an oxygen-free environment at high temperature. This process takes place in the form of separations at C-C or C-H bonds. This process is divided into three parts: hydro cracking, catalytic cracking and thermal cracking. The amount of product produced depends on the method used and the reaction parameters. For example, solid product is obtained at low reaction rates at low temperatures and more liquid product is obtained by cracking operations performed in a short time with rapid temperature increase.

In the pyrolysis process, although the fuel properties of vegetable oils approach to diesel fuel properties, high energy consumption is the most important disadvantage [9].

The pyrolysis method is a good method for the evaluation of industrial wastes and urban wastes besides obtaining fuel. Pyrolysis is also an easy and efficient method among other methods [11].

3.4.Transesterification Method

Transesterification is the most common way to produce biodiesel. Transesterification is the general term used to describe the conversion of one ester to another by exchange of alkoxide groups, the class of important organic reactions in which one ester is being converted. Of all alternatives, transesterification is considered the best choice because it is relatively simple for this process [12].

Biodiesel is obtained from vegetable oils by transesterification reaction (alcoholysis). In the transesterification reaction, the oil is esterified with a mono hydric alcohol (ethanol, methanol), giving fatty acid esters and glycerin as the main product in the presence of catalyst (acidic, basic catalysts and enzymes). In addition, in the esterification reaction diglycerides and monoglycerides, excess reactants and free fatty acids are formed. Rapeseed, sunflower, soy and used frying oils, methanol as alcohol, alkali catalysts (sodium or potassium hydroxide) as catalysts are preferred as biodiesel production. Animal oils can also be used in biodiesel production [13].

Figure 2 shows the transesterification reaction. The triglycerides, the main component of the oil, are converted to mono alkyl esters in the transesterification process. Di- and monoglycerides, excess reactants and free fatty acids are formed as by-products in the esterification reaction. Rapeseed, sunflower, soybean and used frying oils, methanol as alcohol, alkali catalysts (sodium or potassium hydroxide) as catalysts are preferred as biomotor production. Animal fats can also be used in the production of biomotorin. Therefore, the refining stage becomes important. Production is very easy. The degree of purity of biodiesel is the most important point in production. Therefore, the refining stage is very important. Biomotor should be produced over 99% pure. In the transesterification reaction, the main product is esterified with oil, ethanol, methanol, acidic, basic catalysts and fatty acid esters and glycerin in the presence of enzymes.

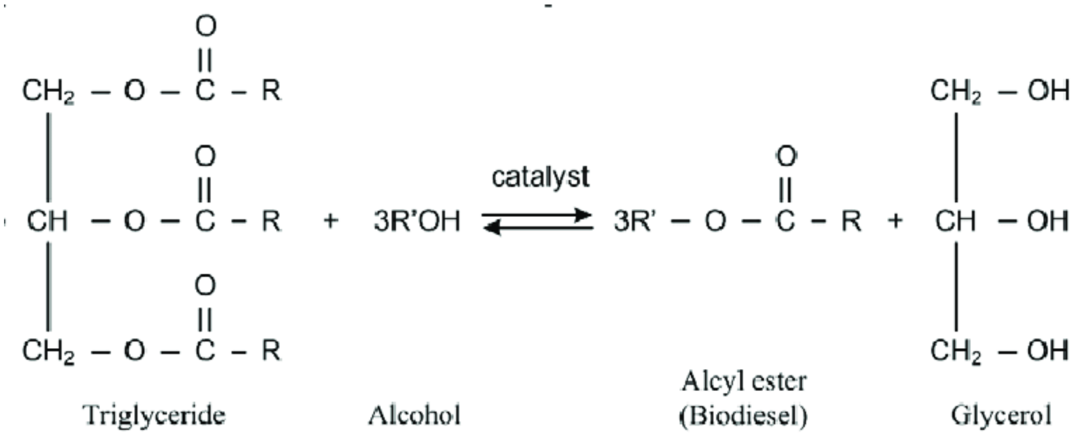

Figure 2: Transesterification Reaction [5]

There is no difficulty in production technology. The most important point in production is the degree of purity of biodiesel. Therefore, the refining stage becomes important. By direct esterification of fatty acids, fatty acids are converted to fatty acid esters with the homogeneous or heterogeneous catalyst effect of acidic character with alcohol and water is released as well as biodiesel. Since water is more volatile than fatty acid esters, it is possible to achieve very high conversions when removed from the reactor by any method [13].

There are 3 main ways to produce biodiesel from vegetable oils or fats:

- Transesterification with base catalyst
- Acid catalyst transesterification
- Fat is converted to fatty acids and then converted to biodiesel.

The base catalyst transesterification process is most commonly used for biodiesel production. Lower temperature and pressure, minimum side reactions and reaction time and high percentage of conversion (98%), direct conversion to biodiesel without intermediate compounds, no foreign, external substances in the structure are among the reasons [9].

4.Studies Related To Biodiesel

Brito et al., Evaluated the potential of advanced oxidative processes (AOP) in biodiesel wastewater treatment. The efficiency of four AOPs, Fenton, photo-Fenton, solar photo-Fenton and sun-photolysis, was tested by measuring the total organic carbon removal from this residue. Also, the toxicity of the treated residue was investigated by fish embryo tests (FET). Solar photolysis (8 hours exposure to sunlight) has been considered the best treatment, while photo-Fenton, similar to solar photo-Fenton and solar photolysis, leads to reduced organic load. This has been studied in relation to significant organic load reduction (more than 92%) which is easily occurring and a 100% reduction in toxicity for Zebrafish embryos in the dilution range has been studied. In the best cases, about 6-8% of the organic content in biodiesel wastewater is pollutant [14].

Keera et al., investigated the variables affecting the yield and properties of biodiesel produced from vegetable oils The variables studied were reaction time (1-3 hours), catalyst concentration (0.5-1.5% w / w) and oil / methanol molar ratio (1: 3-1: 9). The best yield percentages were obtained using a methanol / oil mole ratio of 6: 1, sodium hydroxide (1%) as catalyst and a temperature of 60 ± 1 ° C for 1 hour. Fatty acid methyl ester (FAME) yield was determined by HPLC and FAME compound by gas chromatography. Biodiesel samples were physicochemically characterized. The results indicate that the biodiesel fuel produced is within the recommended biodiesel fuel standards [15].

Elangoa et al. produced batch-scale biodiesel using castor oil by alkali catalyzed transesterification. Initially, the transesterification parameters such as reaction time, catalyst concentration, reaction temperature and methanol molar ratio in oil: biodiesel production were optimized by the conventional method followed by the statistical-based central composite design method. According to optimized experimental results, 95.9%, 1.25% (w / v) KOH catalyst and a 1:12 oil: methanol mole ratio of 94.9% FAME yield were obtained for 60 minutes reaction. The predicted yield is 93.7%. Purification of crude biodiesel was carried out by simple evaporation and silica gel adsorption. Analytical results showed that significant amounts of methyl ester groups, such as ricinoleic, linolenic, palmitic acid and oleic acid, were present in the biodiesel [16].

The use of ultrasound in biodiesel transesterization Ho et al. Reviewed the developments obtained from different raw materials by using acid, base and enzyme catalysts for ultrasound assisted biodiesel transesterization. For each of these, a critical assessment of the state of the art technology has focused on the use of ultrasound energy with heterogeneous catalysts. For each of the technologies studied, the reaction parameters and interactions between process efficiency and productivity are discussed and analyzed [17].

Wu et al. developed a new reaction system for the production of biodiesel by base catalyzed transesterization. Bentonite is used as an adsorbent in a conventional homogeneous base catalyzed transester reaction reaction system to form a heterogeneous system that increases reaction homogeneity. By studying the effect of bentonite on NaOH catalyzed methanolysis of soybean oil and the associated reaction mechanisms, it was found that a suitable bentonite input could support methanolysis. By the rapid removal of water from the system, bentonite enhances the conversion of NaOH to catalytically active methoxide species and the major side reactions can be significantly inhibited. The methanolysis of the triglycerides took place in the liquid phase rather than in the solid phase. The introduction of bentonite also reduced the soap concentration in crude biodiesel; this was useful for producing resinous biodiesel after treatment [18].

Navas et al. emphasize the support of CaO, MgO and ZnO on both mass and C-Al_2O_3, as well as the catalytic activity and characterization of transesterification of soybean oil and castor oil with methanol and butanol. XRD, SEM, CO_2 adsorption followed by TGA and N_2 adsorption were used to characterize the prepared catalysts. The presence of C-Al_2O_3 in the supported catalysts improves alcohol degradation in the superficial basic regions. The first step of the reaction mechanism is then preferred (hydrogen abstraction). In transesterification of butanol with castor oil, MgO / C-Al_2O_3 and ZnO / C-Al_2O_3 catalysts showed high yields to FABE (97% and 85%, respectively). These latter catalysts provide an effective alternative to obtain second generation biodiesel, considering that castor oil cannot be a source and butanol is an alcohol obtainable from biomass [19].

Tiwari et al. studied waste oil transesterification using alkali (NaOH) as catalyst, yielding 85% ester (biodiesel) conversion [20].

In the biodiesel pilot plant, Hüseyin et al. used corn oil, chicken oil and animal oil as vegetable oil to produce methyl ester. When the FFA level of corn oil is below 1%, animal oils are too high to produce biodiesel through the base catalyst. For this reason, since pretreatment reaction was required for animal fats, sulfuric acid was used as catalyst and methanol was used as alcohol in pretreatment reactions. After lowering the FFA level of animal fats to less than 1%, the transesterification reaction was completed with alkaline catalyst. Due to the low FFA content of corn oil, it was subjected to direct transesterification. Potassium hydroxide was used as catalyst and methanol was used as alcohol for transesterization reactions. The fuel properties of the methyl esters produced at the biodiesel pilot plant were characterized and compared with EN 14214 and ASTM D6751 biodiesel standards. According to the results, the ester yield values of animal fat methyl esters are slightly lower than corn oil methyl ester (COME). The production cost of COME is higher than the cost of animal fat methyl esters because it is a high cost biodiesel raw material. Produced methyl esters have similar fuel properties. In particular, the sulfur content and cold flow properties of COME are lower than those of animal fat methyl esters. The measured fuel properties of all produced methyl esters met ASTM D6751 (S500) biodiesel fuel standards [21].

İbrahim et al. investigated the experimental optimization of ultrasound-assisted biodiesel production in the presence of heterogeneous catalyst. Three catalysts; For comparison, CaO, calcined dolomite and calcium diglyceroxide (CaDG) were considered. The D-optimal test plan was subsequently applied to obtain the regression models used to determine the optimum process conditions. The maximum biodiesel yield was calculated as 98.7%, 95.9% and 86.3% for CaO, calcined dolomite and CaDG, respectively. Finally, in the case of CaO catalyst, catalyst loading: 5.35% (oil by weight), methanol / oil ratio: 7.48, ultrasonic power: 40 W, time: 150 min and reaction temperature: 60 ° C yielded maximum biodiesel yield (99.4%) It was [22].

Pali et al. Explorated and developed an indigenous fuel from abundant forest of India. Single stage base catalyst transesterification was employed for biodiesel production. Sal seeds was used biodiesel production in India due to its low acid value. Cetane number, viscosity, calorific value and cold filter plugging point (CFPP) were optimized using response surface methodology (RSM). Methanol to oil molar ratio (3–15:1), KOH catalyst concentration (2.5–15 g/kg), reaction time (30–120 min) and reaction temperature (50–70 °C) were optimized. Results were validated through the confirmation trails and all properties of Sal biodiesel are well within ASTM limits. The results showed that Sal seed is the needed source of biodiesel in India [23].

Zahan and Kano's article discusses the properties of biodiesel, the difference between palm-biodiesel and other biodiesel sources, and the feasibility of using palm oil as a primary source for future alternative and sustainable energy sources. According to the results of the study, it is predicted that the future trends of Palm-biodiesel will likely move towards the balance between the community and market demands and consumer perceptions. With this study, palm oil by-products and mill waste were proposed as future raw materials for biodiesel due to their cheaper costs, availability, abundance, environmental friendliness and minimal effects on food safety. New research is needed to improve product quality and particularly to solve other environmental issues [24].

In the study by Raoufi and Gargari, the optimized lipase A (Lip A) gene from Pseudomonas aeruginosa was fused with GPI's protein Gcw61 and is on the surface of Pichia pastoris X33. Copy numbers of the added lipase gene, actual values are used as 2.09 ± 0.06 by PCR absolute quantification method. Some detergents appear to significantly reduce enzyme activity. The results show that all cell biocatalysts show good potential for the production of biodiesel from microalgae oil in 10 repeat batch cycles [25]

5.Advanced Oxidation Methods And A Case Fenton Process Study From Literature For The Treatment Of Biodiesel Wastewater

In a case study from the lietaruture related to the Fenton Process in order to treat biodisel wastewater four different processes were applied: biodiesel wastewater, Fenton, photo-Fenton, solar photo-Fenton and solar photolysis. The aim is to compare the efficiency of the selected treatment processes and to provide safe alternatives for the disposal of biodiesel wastewater. Fenton and photo-Fenton were performed in triplicate in three sets of glass reactors held under constant magnetic stirring by temperature monitoring. Solar experiments (outdoor) were performed twice and each reactor set was homogenized when [H_2O_2] was added (every 15 minutes). For solar experiments, radiation was monitored using a radiometer (Sunlight, PMA 2120). Prior to TOC analysis, all samples were filled to their original volumes by addition of deionized water (typically 5-10 mL) [14].

5.1.Fenton Reactions

Based on the studies of Grčić et al., 180-minute pre-tests (2014) and Sabaikai et al. (2014) using Fe $^{2+}$ ranging from 20 to 50 mg of L-1 and H_2O_2 to 100 to 1000 mg/L. The best results were obtained using $[Fe^{2+}]$ = 20 mg/L and $[H_2O_2]$ = 1000 mg/L. Based on these results, $[Fe^{2+}]$ = 20 mg/L and $[H_2O_2]$ = 1000 mg/L were used in all other experiments. Experiments using the Fenton reaction were performed in closed glass containers wrapped in aluminum foil. A 100 mL sample was taken from the biodiesel waste water and $FeSO_4.7H_2O$ (FMAIA P.A.) was then added to obtain an iron ion concentration of 20 mg/L. H_2O_2 (Vetec 30%) was added to give a constant concentration of 1000 mg/L every 1000 minutes. The procedure lasted 300 minutes with TOC monitored every 30 minutes [14].

5.2.Photo-Fenton Reaction

This reaction was carried out in 100 mL of biodiesel waste water using the same concentration of iron ions (20 mg L-1) used for the Fenton reaction. Hydrogen peroxide was added every 15 minutes to give a constant concentration of 1000 mg/L. The sample was also irradiated with UV light provided by a high pressure mercury vapor lamp (125 W) (λ = 254 nm). This process lasted 480 minutes and the TOC was measured every 30 minutes [14].

5.3. Solar Photo-Fenton

Experiments were performed using the same conditions as the photo-Fenton reaction (point 2.2.4) but using solar radiation instead of mercury lamp. A 500 mL biodiesel wastewater sample was placed in a glass receiver (29.6 cm x 17.8 cm x 5 cm) and exposed. After the addition of Fe^{2+} (20 mg/L), 1.25 mL of H_2O_2 (1000 mg/L) was added periodically to natural sunlight (outdoor) and every 60 minutes. The experiment lasted 480 minutes (in May 2016 in Midwestern Brazil). TOC content was measured every 60 minutes [14].

5.4.Solar Photolysis

These experiments were performed in a similar way to solar photo-Fenton. It consisted of exposing 500 mL of biodiesel wastewater (in a 29.6 cm x 17.8 cm x 5 cm glass receiver) to sunlight for 480 minutes (in May 2016, Central Brazil). The TOC content was measured every 60 minutes. The solar experiments were continued for the next 180 minutes. This step aimed to assess whether the treatment was at its end [14].

6.Conclusion

As a result of literature studies; Although fossil fuels cause environmental pollution in recent years, they are decreasing rapidly as they are alternative energy sources. Therefore, studies have been started on alternative fuels and it has been determined that biodiesel obtained from vegetable and animal oils can be used as an alternative fuel that can be produced from renewable sources. Biodiesel is a non-toxic, biodegradable and renewable diesel fuel that can be easily dissolved in soil without damaging the environment. Transesterification, a chemical process that converts vegetable oils into an alternative fuel, reduces viscosity. It contains high cetane number, renewable property, high combustion efficiency and low emulsion. Studies on the treatment of wastewater generated during the production of biodiesel are not common, but it is possible to come across in the literature. Fenton, which uses advanced oxidation processes for the treatment of this wastewater, has also been demonstrated. However, further studies are needed to establish effective methods for wastewater treatment.

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