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Various Pre-Treatment Methods to Reduce Free Fatty Acid Content in Non-Edible Vegetable Oils for Biodiesel Production

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In this work, the efforts were made to reduce high free fatty acid (FFA) content in non-edible karanja and jatropha vegetable oils below 1 mg KOH/g. The process was optimized in terms of amount of sulphuric acid used in pre-treatment of the studied non-edible oils. Various adsorbents like activated carbon, alumina, alumina-silica, calcined alumina and calcined alumina-silica exhibited significant removal of FFA in a single-stage filtration process. Pre-treatment of test oil with calcined alumina-silica as adsorbent was found to be the most appropriate for the removal of free fatty acids. Ultraviolet-visible spectroscopy (UV) analysis showed that the original composition of test oil was not changed after the pre-treatment process.

Keywords: Non-edible oil, Free fatty acid, Adsorbents, Biodiesel, Methanol to oil ratio.

INTRODUCTION

The use of non-edible and waste vegetable oils for biodiesel production is a promising approach due to its environment friendly and the feed materials, which are renewable in nature compared to crude oil-based diesel. Oils like rapeseed, soybean, sunflower and safflower [1], which are edible in nature have also been used for biodiesel production. Similar attempts have been made for the biodiesel production from non-edible sources like used frying oils, greases, tallow and lard [2]. In India, there is a high annual production of a variety of non-edible oils, which can be used for the biodiesel production to supplement conventional energy sources. Karanja (*Pongamia pinnata*), jatropha and madhuca [3] have been successfully used for biodiesel production. Biodiesel produced from non-edible oils will help reduce the cost of import on crude oil based fuels. Further, India being an agriculture dependent economy, development of such non-edible oil crops will be more economical and feasible [4].

The conventional method for conversion of vegetable oil into biodiesel is transesterification. Transesterification refers to a catalyzed (generally an alkaline catalyst) chemical reaction involving oil or fat and an alcohol to yield fatty acid methyl esters and glycerol. The factors affecting transesterification reaction are alcohol-to-oil ratio, quantity of catalyst, reaction temperature, pressure, time and the free fatty acid (FFA) content in oil. Conversion of vegetable oil into biodiesel by transesterification reaction is complicated if it contains higher amounts of FFA (> 4 mg KOH/g). Free fatty acids present in vegetable oil form soap with alkaline catalyst and prevent the separation of biodiesel produced. Crude karanja oil contains high FFA content and cannot be directly processed with an alkaline catalyst. Earlier, biodiesel have been prepared from low FFA containing karanja oil [5] by direct transesterification using KOH and solid acid catalysts. Process optimization of direct transesterification of low FFA karanja oil has also been studied using a base catalyst [6]. Biodiesel production from high FFA Karanja oil has been carried out using sulphuric acid and KOH catalysts [7].

The stepwise transesterification reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of the excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order [8]. Several aspects including the type of catalyst (alkaline or acid), alcohol-to-oil molar ratio, temperature, purity of the reactants (mainly water content)

and FFA content have an influence on the transesterification reaction.

In present study, the experiments were carried out to optimize the pre-treatment process for reducing the free fatty acid (FFA) content in vegetable oils below 1 mg KOH/g of oil for biodiesel production. The focus of this work is on reaction parameters that affect transesterification reaction in non-edible karanja and Jatropha vegetable oils. Soybean and linseed oils were also taken to make a comparison of test results. The study also includes the analytical testing of test oils using UV spectroscopy and NMR analysis.

EXPERIMENTAL

Potassium hydroxide, sulphuric acid, phenolphthalein indicator, distilled water, methanol, ethyl alcohol, activated carbon, alumina and alumina-silica chemicals were procured from Merck (AR grade). The karanja, jatropha, soybean and linseed oils were purchased from the local market of Kanpur city, India.

General procedure: A high pressure 2 L capacity batch reactor (AmAr Equipments Ltd., India) was used in this study. The reactor was equipped with a PID controller, RTD-PT100 temperature sensor, electrically heated jacket, a cooling water circulation system, magnetic stirrer and a reflux condenser along with other valves and gauges. A valve at the bottom was used for intermediate sampling.

Acid value and free fatty acid determination of various oil samples: Acid value also referred to as acid number, neutralization number or acidity is the mass of KOH in milligrams required to neutralize 1 g of chemical substance. The acid number is a measure of number of –COOH groups present in a chemical compound such as fatty acid or in a mixture of compounds. In this study, acid value was calculated by the standard method as described in Indian standard methods of sampling and test for oils and fats [9]. Normally, the fatty acids reduce the efficiency of triglycerides to get transesterified with alcohol using an alkaline catalyst, because they react with the alkaline catalyst to produce soaps and thus decreasing the yield of methyl esters or even inhibiting the reaction. Depending on the acidity of oil, one or two process steps can be used, where in the first step the FFA level is reduced below 1% by acid-catalyzed esterification, while in the second step triglycerides present in the product obtained from the first step are transesterified with methanol using an alkaline catalyst to produce methyl ester (biodiesel) and glycerol. Acid value and FFA were calculated by eqns. 1 and 2, respectively.

$$\text{Acid value} = \frac{56.1 \times \text{Titrated value} \times \text{Normality of KOH}}{\text{Sample weight}} \quad (1)$$

$$\text{Free fatty acid (FFA)} = \frac{\text{Acid value}}{1.99} \quad (2)$$

Pre-treatment of oil using sulphuric acid: Feedstocks containing 5-30% acidity or even higher need to be first pre-treated by acid-catalyzed esterification, which could reduce the FFA content prior to transesterification [10]. Pre-treatment was done in the crude oil to reduce the FFA concentration below 1% [11]. The process was intended to convert FFA into esters using an acid catalyst (1% w/w H_2SO_4). Phase separation of the product mixture was done in a separating funnel. Two layers were visible, of which the top layer was taken out and washed with lukewarm distilled water. A schematic diagram of the acid-catalyzed pre-treatment process is given in Fig. 1. Reaction temperature of 60 ºC was found to be the most appropriate for complete esterification of oil.

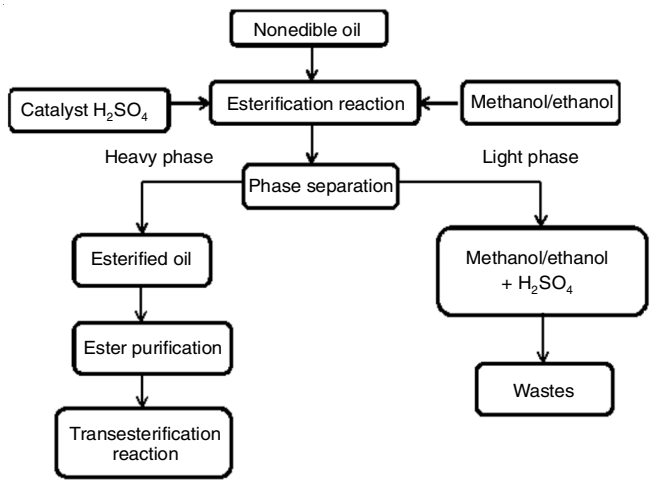

Fig. 1. Pre-treatment of oil by acid-catalyzed process

Effect of methanol-to-oil ratio: The reduction in acid value or FFA concentration is influenced by the quantity of methanol used in the reaction. The study conducted on Jatropha oil initially containing 15% FFA, the concentration was reduced to 10% FFA at methanol-to-oil ratio of 10% w/w and further reduced to 1% FFA at 70% w/w of methanol-to-oil ratio. Further increase in the methanol amount had no significant effect on acid value or FFA concentration largely due to the presence of water produced during the esterification of fatty acids. Practically, the esterification process might be improved by continuous removal of water from the reaction mixture. Therefore, an optimum quantity of methanol was required to complete the esterification of all FFAs present in oil.

Two-stage pre-treatment process: A two stage pre-treatment method has been developed to form methyl esters from various oils by reducing the high FFA content of oil. The first stage requires about 0.4% v/v of methanol-to-oil, while the second stage requires about 0.35% v/v of methanol-to-oil in presence of an acid catalyst, usually 1% v/v H_2SO_4, with continuous stirring at 60 ºC [12]. After the reaction, the mixture was allowed to settling time for 1 h to form the top layer of methanol-water mixture, which is separated. The bottom layer with FFA below 1% was further subjected to transesterification.

Pre-treatment of oil using adsorbent: Activated carbon, alumina and alumina-silica were used for reduction of FFA. It is more simple technique but it takes comparatively longer time for filtration through powder bed made with different quantities of adsorbents.

UV analysis: UV-Vis-NIR spectrophotometer (VARIAN Cary 5000) was used for this analysis in the range of 200-500 nm.

RESULTS AND DISCUSSION

Acid value and free fatty acid determination of various oil samples: Oil sample (7 g) was taken in a conical flask, then freshly neutralized ethyl alcohol and 2 mL of phenolphthalein was added. A 50 mL ethyl alcohol was added into mixture to slow down the reaction. The mixture was then heated to 60 ºC for 5 min and titrated with 0.1 N KOH solution. The oil mixture colour was changed from colourless to pink. The % FFA content of various pure oils is shown in Table-1.

TABLE-1
% FFA VALUE OF DIFFERENT OIL

Pure Oil	Palm	Karanja	Jatropha	Linseed	Soybean
FFA (%)	24	5.78	2.42	0.44	0.19

Free fatty acid (FFA) reduction was carried out by acid pre-treatment method, 30% w/w methanol-to-oil ratio was considered in the reaction mixture. For which 50 mL oil was taken and 17.5 mL of methanol were mixed in a beaker, 0.5 mL H_2SO_4 (1% by volume of oil) was added as catalyst and the reaction was carried out on hot magnetic plate at 60 ºC for 1 h. It was observed that mixture was changing its colour as time increases. The final mixture was kept overnight in a separating funnel for separation. The top layer comprising methanol-water mixture was removed. The bottom layer having FFA below 1% was further subjected to transesterification. From the bottom layer reduction in FFA was checked by using same titration method.

The same experiment was repeated with varying volumes of sulphuric acid and hydrochloric acid. Results obtained with sulphuric acid are shown in Table-2. The experiments performed with 0.25 mL and 3 mL HCl showed no significant change, instead the mixture became viscous and showed the entirely different properties.

TABLE-2
EFFECT OF H_2SO_4 ON REDUCTION OF KARANJA OIL FFA

H_2SO_4 amount (mL)	0.0	0.25	0.5	1.5	3.0
FFA (%)	5.78	5.2	3.99	3.37	4.48

Pre-treatment of karanja oil with H_2SO_4: There were no pre-treatment required for oil having FFA content less than 1% as shown in Table-3; even the added acid increased the acid value of oil.

TABLE-3
EFFECT OF PRE-TREATMENT BY H_2SO_4
ON FFA CONTENT OF DIFFERENT OILS

Oil	FFA % (initial)	Amount of H_2SO_4 (mL)	FFA % (final)
Karanja	5.78	0.5	3.99
Jatropha	2.42	0.5	3.11
Linseed	0.44	0.5	1.196
Soybean	0.19	0.5	No end point

Pre-treatment of oil using activated carbon: Filtration column (1 cm diameter and 20 cm length) was filled with different amount of activated carbon powder. A known amount of karanja oil (20 g) was poured into column and setup was kept until complete filtration. The oil filtrate was collected in drop-wise manner from bottom in another beaker and its FFA was measured using KOH titration method. The experiments were carried out using varying quantities of activated carbon with same amount of oil in each column. Results of experiments are shown in Table-4. The simple filtration with activated carbon is also showing positive result on reduction of FFA of karanja oil. Further increase in adsorbent amount would reduce the FFA significantly, but it would take very high filtration time (more than 30 h).

TABLE-4
EFFECT OF ACTIVATED CARBON ON
REDUCTION OF KARANJA OIL FFA

Activated carbon (g)	0	2	4	6
Karanja oil FFA (%)	5.78	4.3	3.73	2.96

Pre-treatment of oil using alumina and alumina-silica: Alumina and alumina-silica were also shown to have adsorbent property in a previous study [13]. Both having more porous structure and were successfully used for the reduction of FFA. Both adsorbents exhibited greater reduction of FFA than the activated carbon. The procedure followed is the same as done with activated carbon, but the filter bed weight was 4.0 g for both alumina and alumina-silica. As observed alumina is preferred over alumina-silica as it reduces FFA significantly in single filtration (Table-4). Pre-treatment of oil using calcined alumina and calcined alumina-silica was expected to provide better results than uncalcined one; it may be due to removal of moisture at high temperature, which leads to increase the porosity in crystals. For calcination, alumina and alumina-silica powder were kept in furnace at 500 °C for 6 h. Then powdered calcined alumina and alumina-silica were used as adsorbents and oil was passed through adsorbent bed. The filtration was carried out using different weight of adsorbents in filter beds (2, 4 and 6 g) with 20 g amount of oil. The results for experiments carried out with karanja oil (FFA 5.2) are shown in Table-5.

TABLE-5
REDUCTION IN FFA OF KARANJA OIL WITH
VARYING QUANTITIES OF DIFFERENT ADSORBENTS

Name of adsorbent	FFA (%)
Activated carbon (4 g)	3.73
Alumina (4 g)	0.80
Alumina-silica (4 g)	2.72
Calcined alumina (2 g)	3.36
Calcined alumina (4 g)	0.72
Calcined alumina (6 g)	0.68
Calcined alumina-silica (2 g)	2.47
Calcined alumina-silica (4 g)	0.40
Calcined alumina-silica (6 g)	0.17

It is evident from Table-5 that with increase in the amount of adsorbent the FFA of karanja oil decreases. Calcined adsorbents are better than the normal adsorbents. All these results correspond to single stage filtration and leads to significant drop in FFA value. Same experiments were performed on

jatropha oil (FFA 2.42%) using 4.0 g alumina-silica and the FFA value was reduced to 0.074%.

Reaction with homogeneous catalyst: The possibility of biodiesel production with homogeneous base catalysts such as NaOH or KOH was explored using soybean oil (FFA less than 1%). Similar reaction could also been performed using pre-treated oil (FFA < 1%). The optimum quantity of base catalyst was found to be 3.5% w/w of oil. Homogeneous base catalysts have some drawbacks, as these catalysts are soluble in methanol, hence they cannot be reutilized like heterogeneous catalysts. The homogeneous base catalysts favour the formation of stable emulsions, which makes the separation of methyl esters more difficult. In addition, glycerol obtained as an aqueous solution is of relatively low purity [14]. These problems can be alleviated to some extent using heterogeneous catalysts. There is an increasing interest in the possibility of replacing the homogeneous alkaline hydroxides, carbonates or metal alkoxides by heterogeneous solid catalysts insoluble in methanol that could potentially lead to easier rening of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs [15]. In present study, transesterification reaction was carried out using base catalyst with various methanol-to-oil ratios at 60 ºC and 750 rpm. ^{1}H NMR analysis of samples at different time intervals was analyzed and following results were obtained [16,17]. As shown in Fig. 2, the reaction rate was very high and the reaction was completed within 1 h.

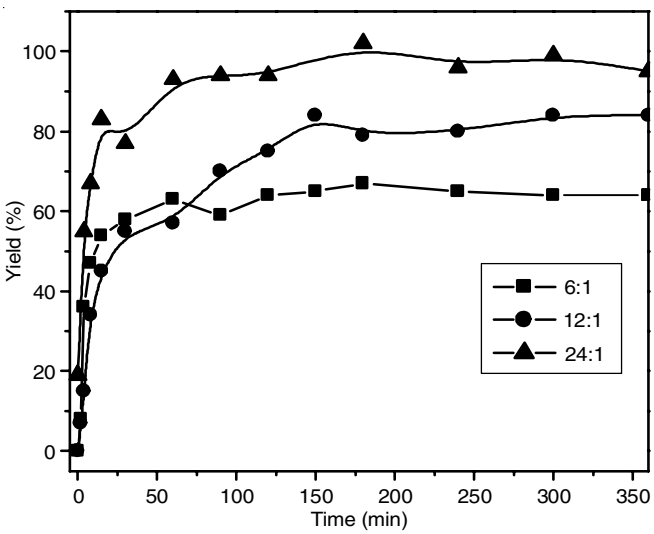

Fig. 2. Effect of methanol-oil ratio on homogeneous catalyzed transesterification reaction

UV studies: UV spectroscopy analysis of oil was done to perform the comparative study of oils as well as pre-treated samples. In UV spectrum (Fig. 3), the peaks of same nature represent the similar components in oils, whereas the different absorption intensities correspond to the different percentages of components. Similar results were found in previous studies [18].

The UV spectroscopy analysis of karanja oil pre-treated with adsorbent alumina and alumina-silica was done (Fig. 4) and peaks similar in nature as shown in Fig. 3 were observed. For karanja oil, the absorption intensity were observed even

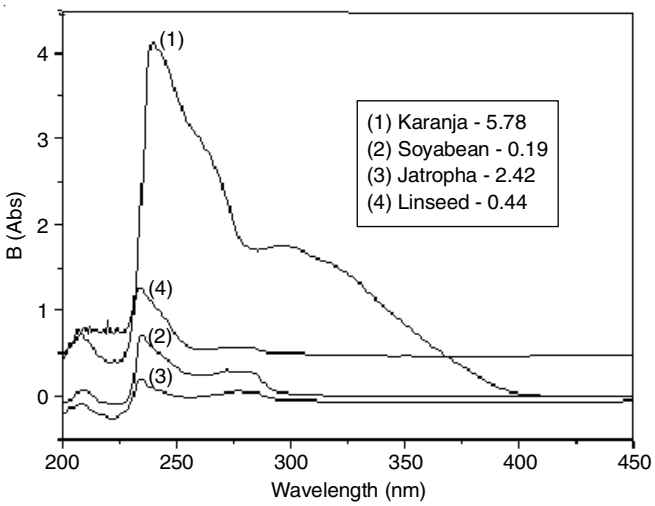

Fig. 3. UV spectroscopy analyses of different oils

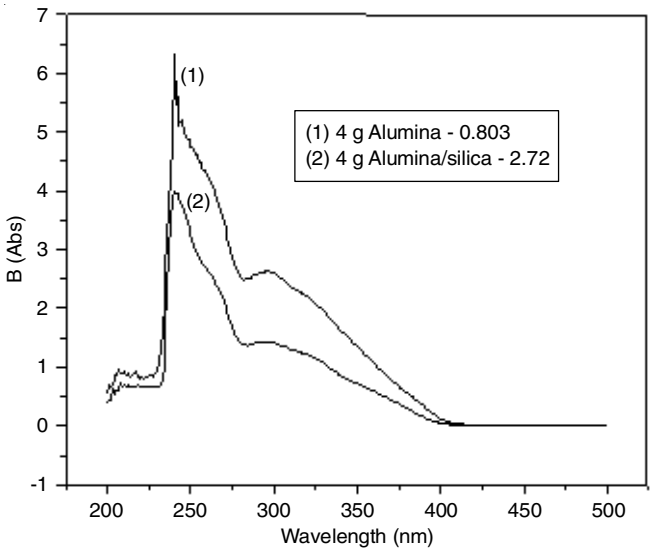

Fig. 4. UV spectroscopy analysis of pre-treated karanja oil with adsorbents alumina and alumina-silica

higher than Fig. 3 as the purity of oil increases in terms of composition.

UV spectrum of pre-treated karanja oil with calcined alumina and alumina-silica have the similar nature of peaks at the same wavelength. However, calcined adsorbents were found to have greater removal of free acids without disturbing the constituent components of the parent oil. The UV analysis of pre-treated karanja oil with activated carbon powder (Fig. 5a) also demonstrated the similar nature of the UV profile (as in Fig. 5b) maintaining the original oil structure.

The comparative plots of all pre-treated oils with 4 g amount of calcined and uncalcined adsorbents are shown in Fig. 6. The original structure of oil remains same even after pre-treatment of oil. The UV profile of different source of oil (different % FFA) could not correctly represent the % FFA in oil, however analysis represents the presence of similar components in the oil.

Conclusion

The free fatty acid (FFA) present in vegetable oil brings negative impact on the transesterification reaction for biodiesel

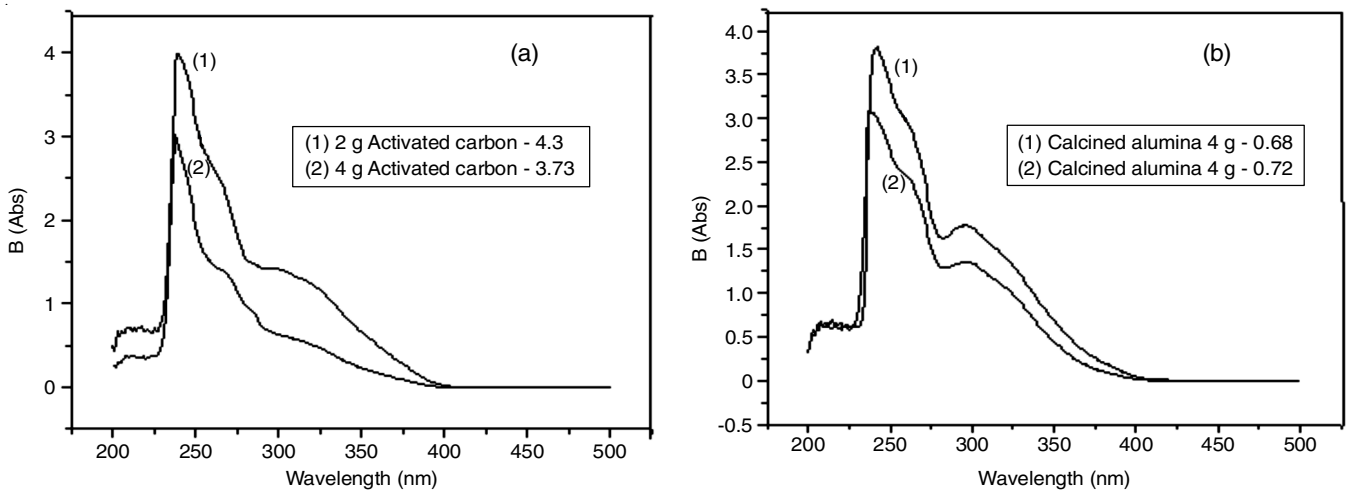

Fig. 5. UV spectroscopy analysis of pre-treated karanja oil with (a) adsorbent activated carbon, (b) adsorbents calcined alumina and calcined alumina-silica

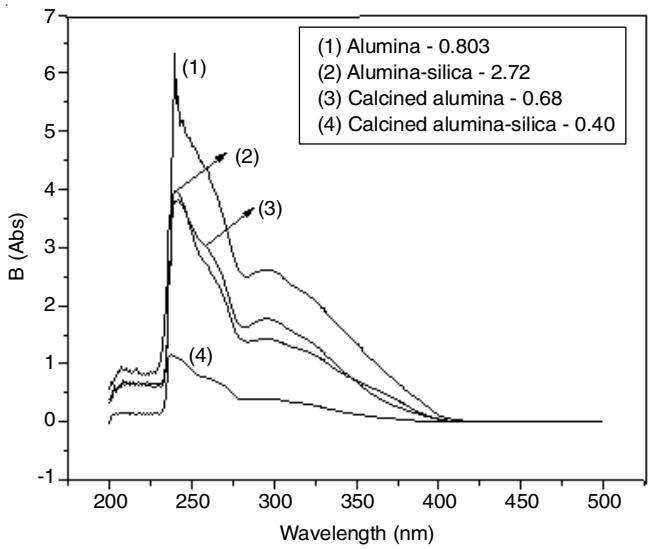

Fig. 6. Comparative UV analysis of pre-treated karanja oil with different adsorbents

production. Various methods were optimized for the removal of FFA present in non-edible oil in present study. The FFA oil was calculated using titration method. The amount of sulphuric acid used as acid catalyst decreased the fatty acid content significantly in karanja and jatropha oil. The process was optimized in terms of amount of sulphuric acid added for pre-treatment of non-edible vegetable oil. Various adsorbents like activated carbon, alumina, alumina-silica, calcined alumina and calcined alumina-silica also triggered the significant removal of FFA in a single stage filtration process. Pre-treatment with calcined alumina-silica as adsorbent taking 6-20 g oil was found to be most appropriate for removal of free acids. The UV analysis revealed that the natural configuration of oil was not altered due to pre-treatment process.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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