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Time Factor in Microwave-enhanced Biodiesel Production

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Abstract: - Cooperative global efforts are held to confront climate change threats by measures aiming at the stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Biodiesel is a renewable, energy efficient, substitution fuel which reduces net carbon dioxide emissions. By running on biodiesel, vehicles can help reduce GHGs and polluting emissions even more, without impairing their performance or reducing their energy efficiency. Biodiesel production is worthy of continued study and optimization of production procedures due to its environmentally beneficial attributes and renewable nature. While the transesterification process for production of biodiesel is well established, there remain considerable inefficiencies in existing transesterification processes. Application of radio frequency microwave energy offers a fast, easy route to this valuable biofuel with advantages of enhancing the reaction rate and improving the separation process. The methodology allows for the use of high FFA content feedstock, including used cooking oil; hence it helps to reduce the cost of production which constitutes a major hurdle towards widespread commercialization of biodiesel. This study showed that the optimum reaction time for microwave-enhanced biodiesel production should be highly respected. Exceeding the optimum reaction time will lead to deterioration of both biodiesel yield and purity.

Keywords: -Biodiesel, Vegetable Oil, Transesterification, Microwave, Bioenergy

1. Introduction

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another by interchange of the alkoxy moiety [1]. Transesterification involves stripping the glycerine from the fatty acids with a catalyst such as sodium or potassium hydroxide, and replacing it with an anhydrous alcohol, usually methanol. This yields methyl or ethyl ester (biodiesel) as well as a smaller amount of glycerol, a valuable by-product.

The three basic methods of ester production from oils/fats are the base-catalyzed transesterification, the acid-catalyzed esterification, and enzymatic catalysis. The most commonly used method of which is the base-catalyzed transesterification technique as it is the most economical process [2]. The transesterification reaction is an equilibrium and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst accelerates considerably the adjustment of the equilibrium [3]. Methanolysis with 1% wt. potassium hydroxide catalyst resulted in successful conversion giving the best yields and viscosities of the esters [4]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed [5]. The optimum methanol/oil molar ratio was found to be 6:1 [4].

While transesterification is well-established, and becoming increasingly important, there remains considerable inefficiencies in existing transesterification processes. In conventional heating of transesterification process (batch, continuous, and super critical methanol process), heat energy is transferred to the raw material through convection, conduction, and radiation from surfaces of the raw material. Thus, the conventional heating consumes more energy and take long preheat and reaction time, optimally 1 hour [4], to produce over 95 percent conversion yield biodiesel product.

An alternative energy stimulant, ‘‘microwave irradiation’’ can be used for the production of the alternative energy source, biodiesel. In the electromagnetic radiation spectrum, the microwave radiation region is located between infrared radiation and radio waves. Microwaves have wavelengths of 1mm - 1 m, corresponding to frequencies between 0.3 - 300 GHz. In general, in order to avoid interference, industrial and domestic microwave apparatus are regulated to 12.2 cm, corresponding to a frequency of 2.45 GHz, but other frequency allocations do exist [6]. Microwaves, a non-ionizing radiation incapable of breaking bonds, are a form of energy and not heat and are manifested as heat through their interaction with the medium or materials wherein they can be reflected (metals), transmitted (good insulators that will not heat) or absorbed (decreasing the available microwave energy and rapidly heating the sample) [7]. Microwaves, representing a non-ionizing radiation, influence molecular motions such as ion migration or dipole rotations, but not altering the molecular structure. Polar solvents of low molecular weight and high dielectric constant irradiated by microwaves increase their temperature very rapidly, reaching boiling point in a short time: in this class of solvents the rate of a given reaction is more enhanced. Typical solvents widely employed in microwave chemistry are water, methanol, ethanol, and acetone. In the presence of microwaves, common solvents are found to boil at higher temperatures: for water the difference is about 5oC; 19oC for methanol, up to 36oC was the difference measured for tetrahydrofuran and acetonitrile. These differences were explained with the different mode of energy supply [8]. Microwave irradiation, an unconventional energy source, has been used for a variety of applications including organic synthesis, wherein chemical reactions are accelerated because of selective absorption of MW energy by polar molecules, non-polar molecules being inert to the MW dielectric loss [7]. The application of microwave irradiation in conjunction with the use of catalysts or mineral-supported reagents enables organic reactions to occur expeditiously at ambient pressure, thus providing unique chemical processes with special attributes such as enhanced reaction rates, higher yields, and the associated ease of manipulation.

There are two mechanisms by which microwave energy can interact with a sample. If a molecule possesses a dipole moment, then, when it is exposed to microwave irradiation, the dipole tries to align with the applied electric field. Because the electric field is oscillating, the dipoles constantly try to realign to follow this. At 2.45 GHz, molecules have time to align with the electric field but not to follow the oscillating field exactly. This continual reorientation of the molecules results in friction and thus heat. If a molecule is charged, then the electric field component of the microwave irradiation moves the ions back and forth through the sample while also colliding them into each other. This movement again generates heat. Because the mixture of vegetable oil, methanol, and potassium hydroxide contains both polar and ionic components, rapid heating is observed upon microwave irradiation, and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained. In addition, because the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be, for short times, much greater than the overall recorded temperature of the bulk reaction mixture. In essence, there will be instantaneous localized superheating. Thus, the bulk temperature may not be an accurate measure of the temperature at which the actual reaction is taking place [9]. Microwave heating compares very favorably over conventional methods, where heating can be relatively slow and inefficient because transferring energy into a sample depends upon convection currents and the thermal conductivity of the reaction mixture [10].

Several examples of microwave irradiated transesterification methods have been reported using adapted domestic ovens to use them as flow systems [11] or batch laboratory ovens [12] but only moderate conversions were obtained.. A more recent study used homogeneous catalysis, both in a batch and in a flow system (Hernando et al., 2007). Leadbeater, and Stencel reported the use of microwave heating as a fast, simple way to prepare biodiesel in a batch mode [14]. This was followed by a continuous-flow approach allowing for the reaction to be run under atmospheric conditions and performed at flow rates of up to 7.2 L/min using a 4 L reaction vessel. [9]. In this study, a scientific microwave with advanced vessel technology was used. This allowed fast vessel heating with homogeneous microwave distribution throughout the cavity.

2. Experimental

2.1. Materials

Feedstock

For the purpose of this study, WVO from two different sources was investigated, and neat sunflower oil was used as a reference. The experiments have been run in triplicate; each set of operation conditions was conducted three times, one with neat sunflower oil used as a reference, and twice with WVOs obtained from two different sources, one collected from a house and the other from a popular fast-food restaurant.

The used frying oil collected from the house (domestic waste vegetable oil - WVOD) was sunflower oil used for 3 times at a cooking temperature of 130°C. The used frying oil collected from the fast-food popular restaurant (restaurant waste vegetable oil - WVOR) included sunflower, and canola feedstock. Information gathered from the participating restaurant, showed that the cooking temperature of the oils varied from 170°C. The oils were kept at these temperatures for ten hours per day and were replaced three times per week.

For this research, commercially-available, virgin sunflower oil was chosen as the triglyceride feedstock (neat vegetable oil - NVO) to react with methanol in the presence of potassium hydroxide catalyst. Sunflower Oil is the non-volatile oil expressed from sunflower plant (Helianthus annus) which contains predominantly linoleic acid (polyunsaturates) in triglyceride form.

Alcohol

Methyl, rather than ethyl, ester production was modeled because methyl esters are the predominant product of commerce, because methanol is considerably cheaper than ethanol, and due to the greater ease of downstream recovery of unreacted alcohol [15]. Ethanol has the advantage that it is renewable. It can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols [11,16]. Most of the world's methanol is being produced using natural gas as a feedstock, however, the ability to produce methanol from renewable biomass resources is growing in interest.

In this study, methanol was the alcohol of choice. [Methanol (Analytical) El-Nasr Pharmaceutical Chemicals Co. ADWIC Mwt. 32.04 Assay 99.8%].

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 was mostly used [17,18,19,20,21]. In other studies the optimum ratio was 10:1 [22,23,24].

Catalyst

Among the most commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive, easy to handle in transportation and storage, and are preferred by small producers. Alkyl oxide solutions of sodium methoxide or potassium methoxide in methanol, which are now commercially available, are the preferred catalysts for large continuous-flow production processes [2].

Biodiesel with the best properties was obtained using potassium hydroxide as catalyst in many studies [18,19,21,22,24,25,26,27]. On the other hand, many other studies achieved best results using NaOH [17,23,28,29].

In this study KOH pellets purified Thann-Fransu 1% by wt. were used. Potassium hydroxide should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of the catalyst through interaction with moisture and carbon dioxide. The catalyst was measured only when ready to immediate use to prevent hydration.

2.2. The Microwave Apparatus

The oven used is **Start S (Milestone)** Milestone Inc. (U.S.A.)**.** Normal pressure glass reactor complete with 500 ml flask and reflux condenser. The oven is supplied with a color touch screen controller which enables creation, store and use of time-vs.-temperature or time-vs.-power reaction profiles. The output microwave power is adjustable up to1200 watts, controlled via microprocessor.

2.3. Gas Chromatography Analysis

GC analysis was undergone for all the samples using **Agilent 5975 GC/MS System** Agilent Technologies (U.S.A.).

3. Results and Discussion

3.1. Using the Conventional Technique

To achieve maximum yield of biodiesel using the waste feedstock, the optimum conditions were studied and compared with those produced from a neat vegetable oil [4]. The results of product yield of all experimental runs are summarized in table 1.

Type of Feedstock

Best results were achieved with the neat vegetable oil followed by the domestic waste vegetable oil, and the least results were achieved from the restaurant vegetable oil.

Catalyst Formulation

Higher yields were reported with KOH with all types of feedstock. This was evident by comparing the results obtained from both formulations under the same conditions, i.e. results obtained from exp.1 were compared with that of exp.6 for NVO (96.15 yield % for KOH and 94.73 yield % for NaOH). Similarly, the results for WVOD were 95.79% for KOH and 90.49% for NaOH and for WVOR 94.51% for KOH and 90.14% for NaOH

Catalyst Concentration

The yield percentage was affected drastically by lowering the catalyst concentration under the same conditions (from 96.15 to 82.07 for NVO).

Molar Ratio of Alcohol to Oil

Increasing the alcohol to oil ratio from 3:1 to 6:1 increased the yield percentage (from 88.04 to 96.15 for NVO). However, increasing the ratio to 9:1 has had a negligible effect.

Effect of Temperature

The effect of temperature on the transesterification for the three types of food was studied. The optimum temperature was 65°C. At lower temperatures of 25°C, the process was incomplete.

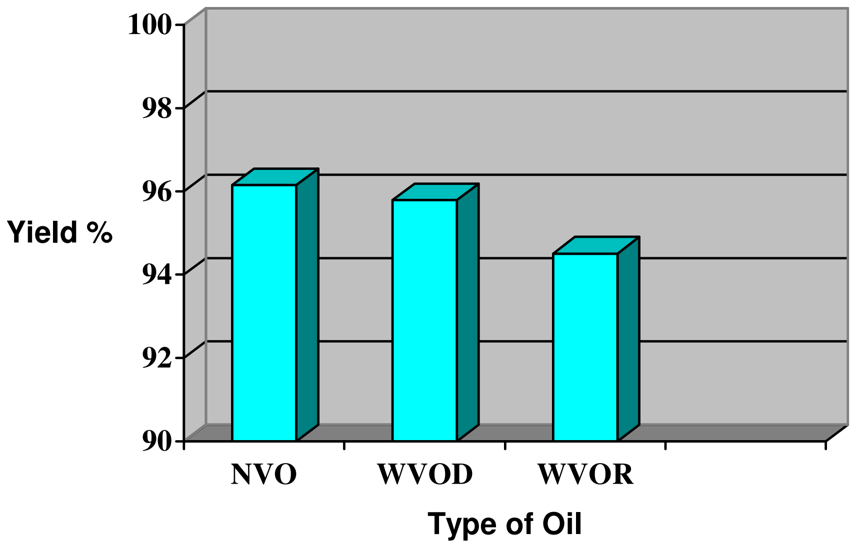
Effect of Reaction Time

Most of the transesterification process was completed in the first 30 min (86.15 yield % for NVO), this was completed to 96.15 after 1 hr. By increasing the reaction time to 3 hrs no noticeable increase in the yield was detected (from 96.15 to 96.30%).

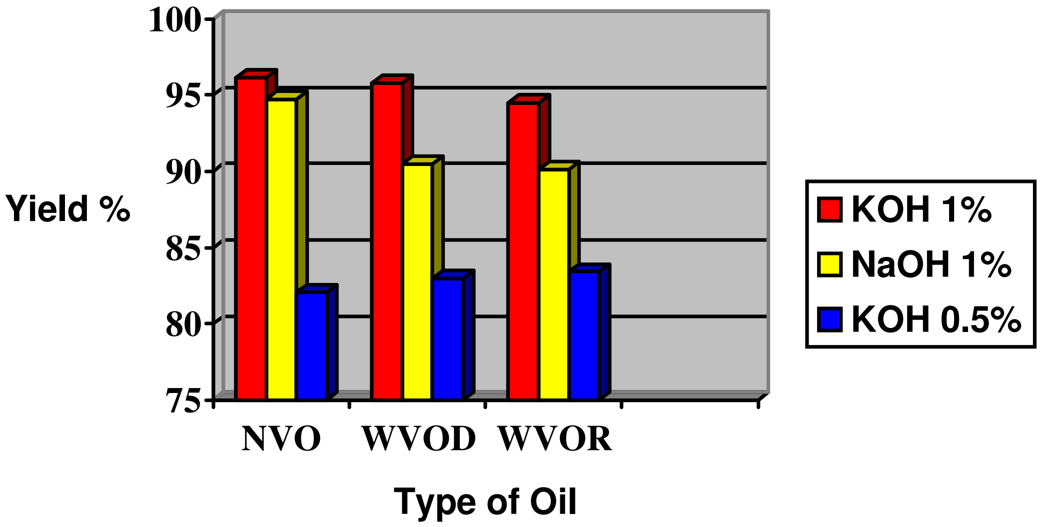
From the obtained results, the best yield percentage was obtained using a methanol/oil molar ratio of 6:1, potassium hydroxide as catalyst (1%), and 65°C temperature for one hour**.** This is depicted in Figure 1.

Table 1. Summary of Experimental Results

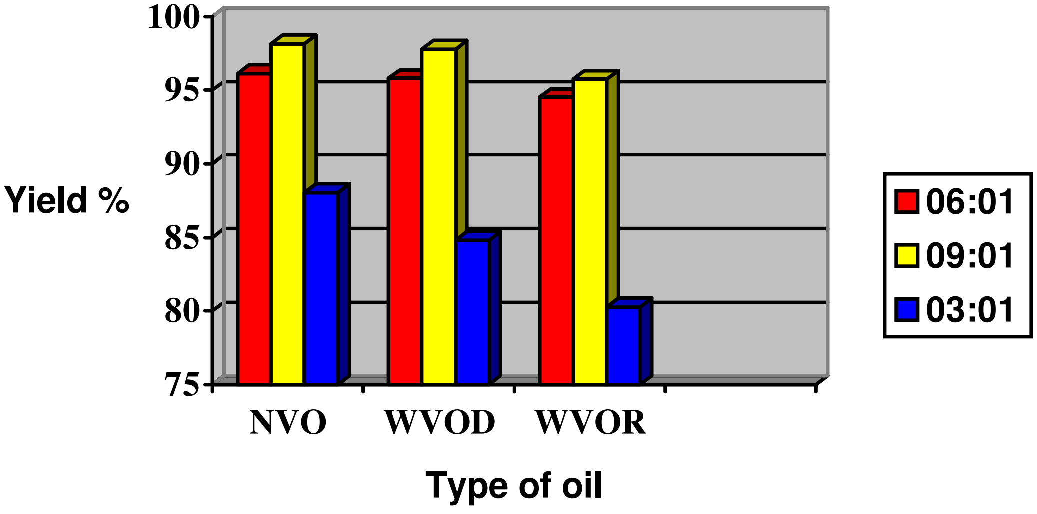
Run	Process Variables						Exp Results
	Feedstock	Catalyst	Catalyst Conc (%wt)	Alcohol/Oil Molar Ratio	Reaction Temp (^{o}C)	Reaction Time (hr)	Yield%
1	NVO	KOH	1	6:1	65	1	96.15
2	NVO	KOH	1	6:1	65	3	96.30
3	NVO	KOH	1	9:1	65	1	98.16
4	NVO	KOH	1	3:1	65	1	88.04
5	NVO	NaOH	1	6:1	65	1/2	86.15
6	NVO	KOH	1	6:1	65	1	94.73
7	NVO	KOH	1	6:1	25	1	75.40
8	NVO	KOH	0.5	6:1	65	1	82.07
9	WVOD	KOH	1	6:1	65	1	95.79
10	WVOD	KOH	1	6:1	65	3	95.94
11	WVOD	KOH	1	9:1	65	1	97.79
12	WVOD	KOH	1	3:1	65	1	84.82
13	WVOD	NaOH	1	6:1	65	1/2	83.50
14	WVOD	KOH	1	6:1	65	1	90.49
15	WVOD	KOH	1	6:1	25	1	71.74
16	WVOD	KOH	0.5	6:1	65	1	83.00
17	WVOR	KOH	1	6:1	65	1	94.51
18	WVOR	KOH	1	6:1	65	3	94.93
19	WVOR	KOH	1	9:1	65	1	95.74
20	WVOR	KOH	1	3:1	65	1	80.28
21	WVOR	NaOH	1	6:1	65	1/2	83.50
22	WVOR	KOH	1	6:1	65	1	90.14
23	WVOR	KOH	1	6:1	25	1	69.15
24	WVOR	KOH	0.5	6:1	65	1	83.43



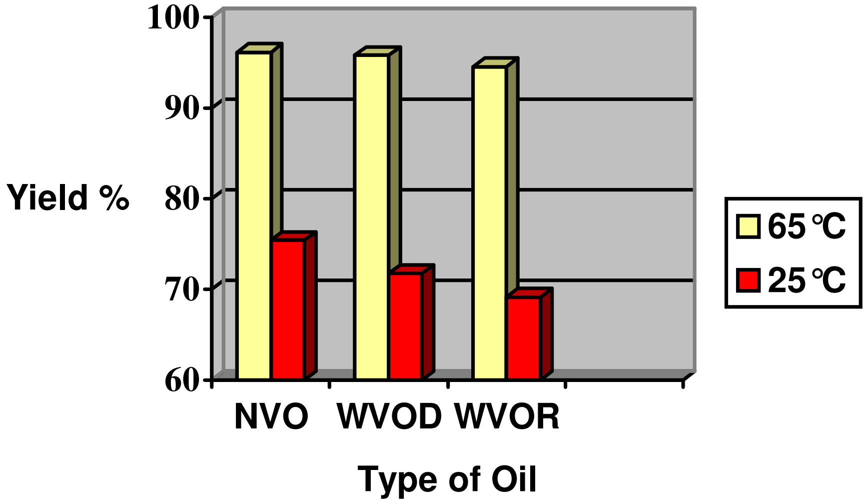
a. Type of feedstock



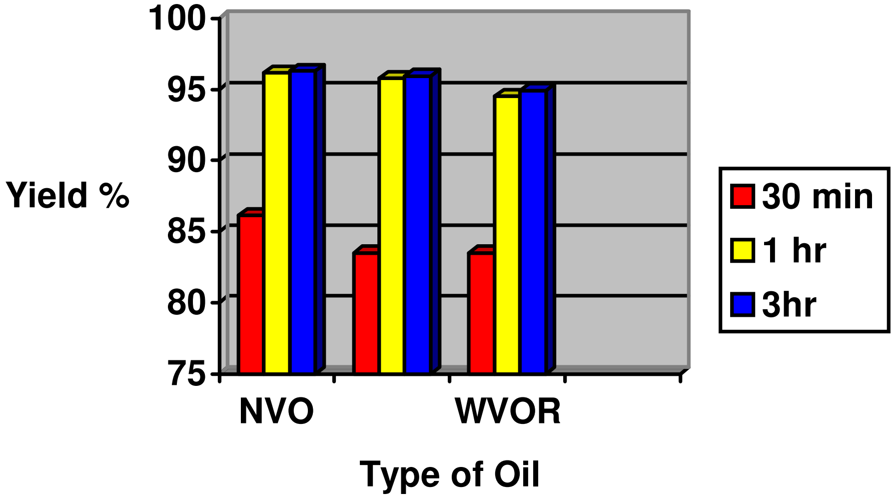
b. Catalyst Formulation and Concentration



c. Alcohol-to-Oil Molar ratio



d. Temperature



e. Time of Reaction

Figure 1. The Effects of the Process Variables on Biodiesel Yield

3.2. Using Microwave Irradiation

The optimum parametric conditions obtained from the conventional technique were applied using microwave irradiation in order to compare both systems. The temperature was adjusted to 65°C, a methanol/oil molar ratio of 6:1 was employed, and potassium hydroxide (1%) was used as a catalyst.

The oil was preheated to the desired temperature of 65°C using the microwave unit. The alcohol–catalyst mixture was then fed into the flask through the condenser. The output power was adjusted to 500 watts and the mixture was irradiated under reflux applying different reaction times.

100% biodiesel yield was obtained by applying microwave irradiation for two minutes compared to one hour with the conventional technique. The static separation time was 30 minutes compared to 8 hours with the conventional technique. No substantial differences were obtained with the different origin of the oil. The results obtained by applying microwave irradiation are summarized in table 2 and figure 2.

Table 1 Effect of Reaction Time on Yield

Time (seconds)	30	60	90	120	150	180	240
Yield %	86.67	90.09	96.48	99.63	76.31	67.47	62.13

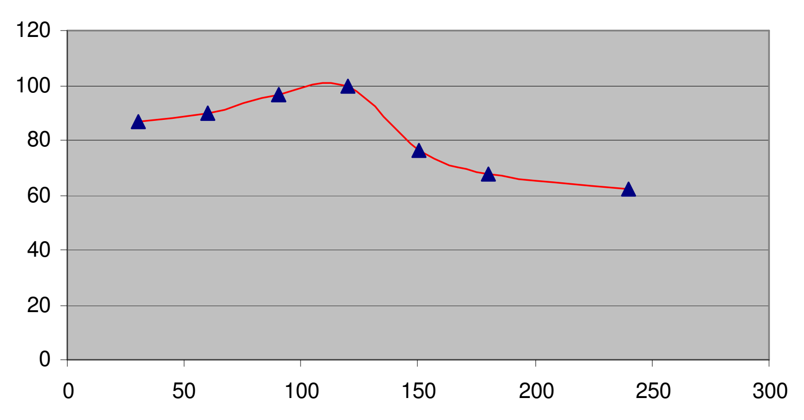


Fig. 2 Effect of Reaction Time on Yield

At reaction times more than 2 minutes, drastic decreases in biodiesel yields were observed. This can be attributed to cracking followed by oxidizing of the formed fatty acid methyl esters to aldehydes, ketones and lower chained organic fractions.

4. Conclusions

Application of radio frequency microwave energy enhances the reaction rate for the conversion of triglycerides to biodiesel, and drives the reaction equilibrium toward the production of biodiesel. Using microwave irradiation also allows the use of high FFA content feed stocks, including animal fats and used cooking oils, in existing transesterification processes by promoting the removal of the fatty acid. Application of radio frequency microwave energy further improves product recovery in the separation of the biodiesel product from alcohol and glycerin in the reaction mixture.

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