

# Biodiesel from Used Frying Oil: A Review

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Received March 02, 2020; Revised April 09, 2020; Accepted April 21, 2020

**Abstract** Disposal of discarded used-frying oils in lakes, rivers and use as feed for animals is a matter of serious concern because it can result in the return of harmful compounds back into the food chain. It is therefore necessary that discarded fried oil is recycled carefully and efficiently. One of the alternatives to recycling is conversion of discarded frying oil into biodiesel. Biodiesel, a fatty acid methyl ester, is a nontoxic biodegradable alternative to fuel (oil/gas). Cooking oil which is discarded after use in food industry can be employed as an economical resource for the production of biodiesel. Biodiesel obtained from discarded frying oil has been found to give better engine performance and lesser carbon emission as compared to other fuels. However, the properties of biodiesel manufactured by using discarded cooking oil are dependent upon the content of free fatty acids, polar compounds and polymerized triglycerides. This review paper covers the key concerns associated with conversion of waste frying oil into biodiesel. In this review paper scientific research and review papers (N=50) were collected via several electronic database such as Medline (Pub-med Version), NLIST (Program of INFLBNET) and DELNET-India (Developing library network).

**Keywords:** biodiesel, used- frying oil, waste-cooking oil, environment, transesterification

**Cite This Article:** Chauhan Pooja, and Suri Sukhneet, "Biodiesel from Used Frying Oil: A Review." *Applied Ecology and Environmental Sciences*, vol. 8, no. 3 (2020): 74-80. doi: 10.12691/aees-8-3-1.

## 1. Introduction

Frying is a popular method for cooking because of the high sensory appeal of fried foods to the consumers. High demand for fried foods, increased consumer awareness regarding food safety and greater surveillance by the food regulatory authorities is concomitantly resulting in more and more accumulation of waste generated from discarded cooking oil. During frying, oil is heated repeatedly at high temperatures (160-190°C) under atmospheric conditions for relatively long duration of time [1]. This results in deterioration of oil. Several physical and chemical changes occur in the oil such as (i) increase in viscosity, (ii) increase in specific heat, (iii) increase in surface tension, and (iv) darkening of colour [2]. The common chemical changes which occur in oils when they are heated repeatedly at high temperature are given briefly in Table 1.

Table 1. Salient chemical changes in oil during the process of frying

Sr. No.	Chemical Reactions	Compounds formed
1	Hydrolysis	Hydrocarbons, ketones, aldehydes, alcohols, esters, lactones, free fatty acids, glycerols, monoacylglycerols, diacylglycerols
2	Oxidation	Alcohols, ketones, aldehydes
3	Poymerization	Dimers, trans-fatty acids, trimers, hetro/ epoxy/ hydroxyl aldehyde

## 2. Used- Frying Oil: Health Concern

Oils undergo three types of reactions during frying, mainly polymerization, oxidation and hydrolysis [3,4]. As mentioned in Table 1, these three reactions result in the formation of several compounds many of which can harm the human body. Certain studies have indicated that regular consumption foods fried in oils with compromised quantity (such as if TPC is more than 25) can increase the risk for the development of chronic diseases, particularly diabetes and liver disorders [5]. Frequent consumption of foods (i.e., four or more times per week) fried in abused oil have been found to increase the risk of cellular damage, growth retardation and hypertrophy of organs such as liver and kidney [6]. In view of strict regulatory standards pertaining to quality of oil to be used for frying, food manufactures are being recommended to discard used cooking oil when the level of total polar compounds reaches above 25 per cent [7]. This has resulted in inappropriate disposal practices.

### 2.1. Used-Frying Oil: Environment Concern

Discarding and recycling of used-frying oil or waste cooking oil (WCO) is a major concern all over the world. European Union produces approximately 700,000-1,000,000 tons WCO annually. It has been estimated that about 40,000 tons of used cooking oil is produced

annually by Asian countries such as India, China, Malaysia, Indonesia, Thailand, Hong Kong, etc. [8,9]. Dumping and pouring of discarded cooking oil in natural water bodies such as lakes, rivers, sea etc. is increasingly becoming rampant. To curb this malpractice and protect the environment many developed countries have set policies that penalize the disposal of waste frying oil through the water drainage system [9,10]. European Union (EU) in 2002 [11] enforced a ban on the use of feeding mixtures containing waste cooking oil for commercial/domestic animals because its use could result in the return of harmful compounds back into the food chain through animal meat. Studies have indicated that use of recycled cooking oils in animal feeds can result in increased risk for several diseases. This is so because WCO contains PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), dioxins and dioxin related substances. These compounds have been found to be present as contaminants in foods of animal origin (milk, meat, poultry, eggs etc.) which enter the human body upon consumption [6]. Thus, WCO should not be used for manufacturing animal feed. It should instead be disposed-off safely or be used in a way that is not harmful to human beings [9].

### 3. Biofuel-a Solution to Recycling Used-frying Oil

The annual consumption of diesel fuel in the United States is 178 million tons and global consumption is 934 million tons [9]. According to the reference [12] shows that, India is the fourth largest energy consumer in the world; oil and gas provide for nearly 35.61 percent of total energy consumption in India. It is expected that by the year 2035, India shall need 1,516 million tons of oil as a primary source of energy which would be nearly 3 times of the current requirement.

Biodiesel is an alternative to other fuels such as petrol and gas. It is a biofuel which is increasingly gaining attention. Biodiesel is a good lubricant; about 66 percent better than petro-diesel [13]. It can be manufactured from used or discarded vegetable oils and animal fats [14]. Discarded frying oil can be recycled and used for the manufacture of biodiesel (monoalkyl esters). The data on the requirement of diesel fuel and availability of waste cooking oil in any country indicate that the biodiesel obtained from waste cooking oil may not replace diesel fuel completely. However, a substantial amount of diesel fuel can be prepared from waste cooking oil [15]. The production cost of biodiesel is very high which may be partially solved by using waste cooking oil as a raw material [16]. According to reference [17] shows that, global production of waste cooking oil is sufficient enough to produce about 10 million tons of biodiesel. Use of biodiesel helps to reduce the emission of carbon dioxide. Further, the use of biodiesel would help to reduce our dependency on fuel imports. Since it is renewable in nature and safer to handle, it is therefore a sustainable source of energy. According to references [6,18] biodiesel obtained from waste cooking oil is most environment friendly as compared to other liquid fuels. Biodiesel has no aromatic compounds, negligible sulphur content, and

oxygen atoms. There is considerable reduction in the emission of carbon monoxide (CO) and tetrahydrocannabinol (THC) upon its combustion as compared to other regular fuels [10].

Government of India in its National Policy on Biofuels [7] has laid stress on increasing the production and use of biofuels. “*Biofuels are liquid or gaseous fuels produced from biomass resources and used in place of, or in addition to, diesel, petrol or other fossil fuels for transport, stationary, portable and other applications*”. They can be produced from Biomass. According to this policy “*Biomass are the biodegradable fractions of products, wastes and residue from agriculture, forestry and related industries as well as the biodegradable fraction of industrial and municipal wastes*”. Used cooking oil is a natural bio degradable resource or biomass which can be utilized for producing biodiesel- a biofuel.

## 4. Methods for Producing Biodiesel from Waste Cooking Oil

Biodiesel is most frequently prepared through the process of transesterification. Transesterification is a process in which primary (linear monohydroxy) alcohols react in the presence of a catalyst with triglycerides of free fatty acids to form glycerol and esters. Transesterification is dependent upon several factors such as reaction temperature, type of alcohol used, rate of agitation, amount of alcohol, and type of catalyst [19]. The triglyceride component necessary for biodiesel production can come from various bio-sources such as edible and non-edible oils including waste and used cooking oils/fats. Commonly used alcohols are butanol, methanol, or ethanol while the catalysts employed can be alkaline, acidic or enzymatic. The choice of catalyst is dependent upon the presence of undesirable compounds especially free fatty acids (FFAs) and water. Subsequent to the transesterification reaction, alcohol esters of vegetable oils are formed. Alcohol esters of vegetable oils have properties similar to those of diesel fuel, and therefore the product formed is known as ‘Biodiesel’. Waste cooking oils are usually vegetable oils which are more viscous than diesel and hence cannot be used as such in a diesel engine. However, the transesterification process helps to decrease the viscosity of waste cooking oils and hence the resultant biodiesel has improved fuel properties [20]. Glycerin is the principal by- product obtained during the transesterification of waste cooking oil and is often used in the soap industry [21].

### 4.1. Catalytic Transesterification Methods

The transesterification reactions can be catalyzed by alkalis, acids or enzymes by heating them with large amount of anhydrous methanol and a catalyst [22,23,24]. They are being discussed below:

#### 4.1.1. Alkali- Catalyzed Transesterification

Alkaline catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (NaOCH<sub>3</sub>) can be used for transesterification of edible oils. Transesterification process carried out by using alkaline

catalyst is much faster than that catalyzed by acidic catalyst because alkaline catalysts are lesser corrosive to industrial equipment [25]. However, the application of an alkaline catalyst in the transesterification of waste cooking oil is limited, because the FFA in waste cooking oil reacts with alkaline catalysts (KOH, NaOH) to form soap. The soap formed during the reaction prevents the separation of glycerol, which reduces the yield of biodiesel. The presence of water in waste cooking oil affects the yield of methyl ester by favoring saponification reaction. Despite these problems many researches are available on alkali catalyst transesterification. Study conducted by reference [25] indicates that when sodium hydroxide is used as a catalyst there is 85 percent yield of biodiesel and the quality of the end product is within the recommended standard values for biodiesel. Several other studies have also indicated similar results and are listed in Table 2 and Table 3.

#### 4.1.2. Acid- Catalyzed Transesterification

Acid catalysts can also be used for transesterification and are usually preferred over alkali- catalysts. Commonly used acid- catalysts are sulfuric acid, hydrochloric acid and sulfonic acid [26,27]. Alkali-catalyzed process is sensitive to the purity of reactants, especially to the presence of water and types of free fatty acids (FFAs) [28]. According to reference [29] has reported that an acid catalyst is insensitive to the type of FFAs present in WCO and is better than the alkaline catalysts especially in case of vegetable oils containing >1 percent FFAs. The only disadvantage of an acid catalyst is a slower rate of reaction. Now-a- days solid acid catalysts are increasingly being used. They have a strong potential to replace liquid acids; eliminating the problem of separation, corrosion and

environment. Solid acid catalysts such as tungsten oxide, molybdenum oxide etc. are commonly being used now a days [30].

#### 4.1.3. Acid- and Alkali-Catalyzed Two-Step Transesterification

Acid and alkali catalysts have their own merits and demerits in the transesterification of waste cooking oil. Therefore, several researchers have used both; acidic and alkaline catalysts, for the production of biodiesel from waste cooking oil. An acid catalyst is usually used first to convert FFAs to the esters and to decrease the FFA level to  $\leq 1$  percent. In the second stage, the transesterification of oil is done by using an alkaline catalyst [31].

#### 4.1.4. Enzyme-Catalyzed Transesterification

Chemical (acid or alkali) catalyzed transesterification of waste cooking oil has several disadvantages, such as pretreatment of feedstock, recovery of glycerol and removal of the catalyst. It is also an energy-intensive process (high stirring speed, and the temperature required for good conversions). Therefore, enzyme catalyzed transesterification is being done. Enzyme (such as lipase) catalyzed transesterification have several advantages over the traditional chemical-catalyzed ones. There is no generation of byproducts, easy recovery of biodiesel, mild reaction conditions, and the catalyst can be recycled. Also, enzymatic reactions are insensitive to FFA and water content in waste cooking oil. In view of these advantages greater work is being carried out in this area. Newer methods of producing biodiesel from cooking oils are being explored such as the co- solvent process and super critical alcohol transesterification process [32,33,34].

**Table 2. Salient researches conducted on production of biodiesel from waste cooking oil**

Author(Year) [Reference]	Types of WCO	Types of transesterification	Yield (%)	Molar ratio	Time(minutes)	Temp (°C)
Gendy et al.(2015) [35]	Sunflower oil	Heterogeneous bio- catalyst produced from eggshell	97.5	6:1	30	60
Akhtar et al.(2014) [20]	Unspecified	Two step acidic- alkali catalyst (Sulphuric acid & Methanol)	84.0	9:1	75	60
Saifuddin et al. (2009) [36]	Unspecified	Enzymatic (lipase) hydrolysis followed by acid- catalyzed transesterification ( sulphuric, hydrochloric, nitric, phosphoric, acetic acid)	88.0	15:1	60	50
Hossain et al. (2010) [37]	Canola oil	Alkali- catalyzed transesterification	49.5	1:1	120	55
Chen et al. (2006)[38]	Unspecified	Enzymatic (R. oryzae lipase)	88-90	4:1	-	40
Hirkude et al.(2014) [39]	Unspecified	Transesterification (Potassium hydroxide)	85.0	6:1	--	--
Jacobson et al.(2008) [30]	Unspecified	Solid acid catalyzed	98.0	18:1	600	200
Refaat et al.(2008) [40]	Sunflower oil	Catalyst transesterification (Potassium hydroxide)	96.15	6:1	60	65

**Table 3. Salient researches conducted production of biodiesel from cooking oil**

Author (Year) [Ref]	Type of oil	Type of transesterification	Yield (%)	Molar Ratio	Time (minutes)	Temperature (°C)
Onukwuli et al.(2017) [41]	Refined cotton oil	Alkali catalyst (Methanol and Potassium hydroxide)	96	6:1	60	55
Akhtar et al.(2014) [20]	Cotton seed oil	Two- step acid- alkali catalyst (sulphuric acid and methanol)	91.7	6:1	60	60
Akhtar et al.(2014) [20]	Rice bran oil	Alkaline catalyst (sulphuric acid)	87.0	6:1	90	55
Hossain et al. (2010) [37]	Sunflower oil	Base- catalyzed transesterification	99.5	4:1	180	40
D'Cruz et al.(2007) [42]	Canola oil	Heterogeneous base catalyst	96.3	6:1	120	40
Sinha et al. (2008) [43]	Rice bran oil	Transesterification	90.1	9:1	60	55

Some of the researches carried out on converting cooking oil/used cooking oil into biodiesel have been summarized in Table 2 & Table 3 respectively. The results of various studies indicate that the yield of biodiesel from waste cooking oil generally ranges from 84.0-97.5 percent while the yield from fresh cooking oil is slightly higher i.e. 87.0- 99.5 percent. The yield from canola oil has been reported to be exceptionally low. The reasons for such low yield need to be reviewed further. It can also be noted from these studies that the duration required for production of biodiesel is longer in case of cooking oil (60min- 180 min) as compared to waste cooking oil (30min-120min) except in case of one study which reports the duration to be 10 hours. As reported, there is no major difference in the temperature required for production of biodiesel from waste cooking oil (40-65°C) or other cooking oils (40-60°C).

## 5. Quality Parameters of Biodiesel

Several studies have indicated that the thermal performance of biodiesel production from waste cooking oil closely resembles that of biodiesel produced from fresh oil. Hydrocarbon emissions of waste cooking oil have been found to be 35 percent lower as compared to emissions from diesel produced from fresh oil [6,35,39]. Standard values for various parameters of biodiesel are given in Table 4 such as density, flash point, cetane number, calorific value and specific gravity. Density of fuel refers to the mass per unit volume, measured in a vacuum at 15°C. Several factors influence density of biodiesel such as molar mass, FFA and water content

of substrate and the temperature used during the transesterification process. The density of fuel directly affects performance of fuel, because some of the properties which affect engine performance, such as viscosity, cetane number and heating value are closely related to density. The density of the fuel also affects the quality of atomization and combustion. Knowing the density is also necessary in the storage, transportation and distribution process of biodiesel as it is an important parameter to be taken into account in the design of these processes. As biodiesel is made up of a small number of methyl or ethyl esters that have very similar densities; variability in their amounts in the feedstock does not affect the density of final product. Thus, a very high value for density of biodiesel could be an indicator of contamination [44]. Another important parameter which is an indicator of biodiesel quality is flash point. According to ASTM-D-93, flash point is the temperature at which a fuel must be heated so that a mixture of the vapor and air above the fuel can be ignited. Although the flash point does not affect combustion directly; higher values make fuels safer with regard to storage, handling and transportation. Flash point varies inversely with the fuel volatility. The minimum flash point prescribed for biodiesel by various countries is 93°C in the United States, 100°C in Brazil and 120°C in Europe. The flash point of biodiesel decreases rapidly as the amount of residual (un-reacted) alcohol increases. Since the flash point of methanol and ethanol is usually between 11-12°C and 13-14°C respectively; thus, the flash point of biodiesel is an indicator of its methanol or ethanol content. The higher their content; lower is the flash point [44].

**Table 4. United States (ASTM) and European Standard values for various properties of biodiesel**

Fuel properties	Standard Values	Organization	References
Density (Kg/m <sup>3</sup> , at 15°C)	860-900	(EN 14214)European standard	Demirbas, [26]
Flash point (°C)	100-170°C	ASTM (D6751) United states	Onukwuli et al., [41]
Cetane number	48-65	ASTM (D6751) United states	Onukwuli et al., [41]
Calorific value (MJ/Kg)	35(min)	(EN14213) European standard	Barbás and Todorut, [44]
Specific gravity at 15.5°C	0.88	ASTM (D6751) United states	Onukwuli et al., [41]

**Table 5. Physiochemical properties of biodiesel produced from waste cooking oil**

Author (year) [reference]	Type of waste cooking oil	Density (g/cm <sup>3</sup> )	Specific gravity (g/cm <sup>3</sup> )	Calorific value (MJ/kg)	Cetane number	Flash point (°C)
Gendy et al. (2015) [35]	Sunflower oil	0.884	0.885	39.37	43	161
Sudhir et al.(2007) [6]	Palm oil	0.870	0.893	39.76	50.54	160
Akhtar et al.(2014)[20]	Unspecified oil	--	0.870	--	55.8	188
Chen et al.(2006)[38]	Unspecified oil	0.890	--	32.00	56.6	171
Dorado et al.(2003) [46]	Olive oil	0.882	--	39.67	58.7	169
Widyan&Shyoukh (2002) [21]	Palm oil	--	0.8737	39.30	--	109
Hirkude et al.(2014) [39]	Unspecified oil	--	0.8700	39.00	--	140

**Table 6. Physiochemical properties of biodiesel produced from fresh cooking oil**

Author (year) [reference]	Types of cooking oil	Specific gravity (g/cm3)	Calorific value (MJ/Kg)	Cetane number	Flash point (°C)
Onukwuli et al.(2017) [41]	Refined cotton oil	0.8817	39.54	56.06	173
Akhtar et al.(2014) [20]	Cotton seed oil	0.8400	--	58	172
Akhtar et al.(2014) [20]	Rice bran oil	0.8600	--	59.5	185
Sinha et al.(2008) [43]	Rice bran oil	0.8700	42.2	63.8	183

Cetane number is also a widely used parameter for checking quality of biodiesel. It measures aromaticity of fuels. Cetane number of biodiesel is influenced by the composition of oil or fat feedstock [45]. Cetane number is a measure of its ignition quality. The cetane number of biodiesel depends on the oil or fat feedstock. Cetane number increases with chain length, decreases with number and location of double bond and changes when the location of the carbonyl group changes in the carbon chain. Calorific value which is a measure of the energy content of the fuel is also a very important property of biodiesel, because it determines its suitability as an alternative to diesel. The calorific value of biodiesel has been found to be comparable with that of diesel. For instance according to a study conducted by reference [43] the calorific value of biodiesel produced from rice bran oil is 42.2 MJ/Kg which is almost 94 per cent of the calorific value of diesel (44.8 MJ/Kg). A slightly lower value could be attributed to the comparatively higher oxygen content of biodiesel. Specific gravity of a fuel determines its performance and hence is used as a quality assessment parameter. The specific gravity of biodiesel is influenced to a great extent by the composition of the feedstock. The specific gravities of biodiesel and diesel have been found to be very similar [45].

Salient researches carried out on converting cooking oil/used cooking oil into biodiesel and the resultant physicochemical properties have been summarized in Table 5 & Table 6 respectively. The results of various studies indicate that specific gravity of biodiesel produced from waste cooking oil generally ranges between 0.873 – 0.893 while the specific gravity of biodiesel obtained from fresh cooking oil is slightly lower i.e. 0.88-0.84. The calorific value of biodiesel produced from waste cooking oil is 32- 39.76 MJ/Kg which is a little lower than the calorific value (39.54 - 42.2 MJ/kg) of biodiesel produced from fresh cooking oil. Cetane number between 48-65 (ASTM D6751) is related to better fuel consumption, horse power, torque and haulage rates. As can be seen in Table 5 and Table 6, the cetane number of biodiesel produced from waste cooking oil is 43- 56.6 which is slightly lower than that of biodiesel obtained from fresh cooking oil i.e. 56.06- 63.80. According to the U.S department of transportation flash point of 93°C or higher is considered to be non-hazardous [45]. As mentioned above in case of biodiesel produced from waste cooking oil flash point ranges from 109-188°C as compared to biodiesel obtained from fresh cooking oil 172-183°C.

## 6. Effects of Various Products Formed in the Frying Process on Biodiesel Quality

Several undesirable substances such as polar compounds are formed due to repeated and prolonged heating/ frying of oil. Reference [3] shows that, refined rapeseed oil was heated at 180°C for  $\geq 20$  hours, due to which the polar content of oil increased above acceptable levels. This, heated rapeseed oil was transesterified with methanol using alkali (KOH) catalyst at room temperature. Analysis of resultant biodiesel by high performance size exclusion chromatography (HPSEC) indicated the presence of dimeric fatty acid methyl esters. This could be attributed to the fact that during heating the polymers formed get

cleaved to result in the formation of monomeric and dimeric fatty acid methyl esters. The formation of these compounds results in increased molar mass and reduced volatility of the biodiesel. Thus, it can be said that the presence of fatty acid esters present in waste frying oil influence the fuel characteristics (such as increased viscosity and reduced burning characteristics), leading to formation of greater amount of Conradson carbon residue (CCR). Higher CCR amount is linearly related to an increase in glycerides as well as FFAs, soaps, remaining catalyst, and other impurities [47]. According to the ASTM standards, the upper limit for CCR value is 0.05 percent. Studies indicate that, in the case of methyl esters obtained from heated rapeseed, as the amount of dimeric and polymeric fatty acid methyl esters increases from 0.7 weight percent to 5.7 weight percent, the CCR value also increases from 0.02 to 0.17 percent [9]. In a study conducted by Reference [3] shows that dimeric and polymeric methyl esters were found to have no negative influence on engine performance in long-term performance tests when 100 percent ester obtained from waste frying oil was used as fuel in two city buses.

To produce biodiesel by transesterification process, the vegetable oil (feedstock) should preferably have an acid value less than 1 and all other materials should be substantially anhydrous. If the acid value is greater than 1, more NaOH or KOH is required to neutralize the free fatty acids. Free fatty acids and water always produce negative effects if transesterification is carried out by alkali catalyst. The presence of free fatty acids and water is related to greater soap formation and higher use of catalyst. It also reduced effectiveness of catalysts [26]. Reference [48] shows that observed during their experimental study that the presence of water can pose a greater negative effect as compared to the presence of free fatty acids and hence the feedstock should be water/moisture free. Thus, if either acid or alkali catalyst is used alone the quality and type of FFAs can have an influence on the quality of resultant biodiesel. The type and amount of FFAs present in WCO however, do not influence the biodiesel quality if transesterification is carried out by enzymatic method or if both acid- alkali catalysts are used together [20,49,50]. Thus, the amount and type of FFAs, polar compounds, and water present in the waste cooking oil, must be taken into consideration during transesterification as they greatly affect the quality of biodiesel.

## 7. Conclusion

Government of India under the Swachh Bharat Abhiyan and the Food Safety and Standards Authority of India under its EEE (Education, Enforcement, Ecosystem) strategy are increasingly emphasizing upon the use/recycling of food waste by employing economically productive and sustainable solutions. Use of discarded frying oil for the manufacture of biodiesel is one possible solution to sustainable development. Production of biodiesel from WCO can address three key concerns viz. health, environment and energy demand. To facilitate this, it is necessary to create awareness among the masses regarding the concept of recycling WCO into biodiesel. There is also need for non-governmental support so that

WCO generated in various food service units and households can be collected and transferred to biodiesel manufacturing units. Intensive research for conversion of waste cooking oil to biodiesel locally and at low cost needs to be given impetus. There is also a need to develop quality standards for production of biodiesel from WCO. International and National support from both public and private sector can be helpful in developing and implementing technologies necessary for effectively producing and utilizing biodiesel from waste cooking oil.

## Conflict of Interest

The authors declare that they have no competing interests.

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