Applicability of used rapeseed oil for production of biodiesel

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Biodiesel is composed of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. It does not contain any petroleum products, but it may be blended with conventional diesel to provide a biofuel that can replace petroleum diesel.

The present production of biodiesel is based mainly on plant oils. Almost all current technologies of conversion of these oils into fuels for diesel engines require high-quality raw materials and a high content of triglycerides. The traditional method of synthesis of fatty acid methyl esters is based on the alkaline-catalyzed transesterification reaction, which has many disadvantages. For example, the reaction is slow and does not proceed to completion. Although waste frying oils can be used, their conversion is complicated if the oils contain large amounts of free fatty acids (FFA) that neutralize the alkaline solution and produce soaps. These soaps can prevent separation of the biodiesel from the glycerin fraction.

In these times of intensive growth in the consumption of fried foods, there arises a problem of handling large amounts of used frying oils. The largest quantities of vegetable oils and fats are being used for production of fried food both by the food industry and in the home. Contrary to the commonly held viewpoint, used frying oil still contains many desirable components, which may be used in several ways. For example, it can be applied as an additive to feeds for farm animals, which enrich the diet nutritionally and make the feed more oily.

Prototype engines capable of burning used frying oil directly have been produced, but most research is being done on the production of methyl esters from the oil to yield biodiesel for subsequent blending with petroleum diesel.

Long recognized for being environmentally friendly, biodiesel is renewable, nontoxic, biodegradable, and sulfur-free,

Idaho researchers explore used fry oil conversion

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(above) Dan Finosar monitors the reaction process. (left) Robert Fox shows a bucket of used frying oil.

As reported in the September 2003 issue of *inform* (*14*: 528–530, 2003), The Netherlands, the United Kingdom, Austria, and several other European countries convert used frying oil to biodiesel. In the United States, where petroleum fuel prices are lower, biodiesel costs more than most consumers are willing to pay. But scientists are exploring processes to economically recycle used frying oil into fuel.

According to the National Biodiesel Board, Jefferson City, Missouri, there are three production methods for producing biodiesel: base catalyzed transesterification of oil, direct acid catalyzed transesterification of oil, and conversion of oil to its fatty acids and then to biodiesel. Most biodiesel production uses the base catalyzed reaction—100 lb (45.4 kg) of oil are reacted with 10 lb (4.5 kg) of a monohydric alcohol such as methanol, which yields 100 lb (45.4 kg) of biodiesel and 10 lb (4.5 kg) of glycerol. The reacted mixture is sometimes neutralized at this step, if needed. The glycerol and biodiesel are separated and the excess alcohol in each is removed. The glycerol by-product is usually a crude grade. The biodiesel often needs to be purified to remove residual catalyst or soaps.

Continuous production

Dan Ginosar and Robert Fox, researchers at the U.S. Department of Energy's Idaho National Engineering and Evionmental Laboratory emitting 80% fewer hydrocarbons, 60% less carbon dioxide, and 50% less particulate matter than petroleum diesel. In fact, a 20% blend (biodiesel 20) with petrodiesel in trucks and buses would eliminate the black smoke (actually, unburned fuel) emitted during acceleration. Biodiesel in the form of esters from waste cooking oils was tested and its emissions were reportedly favorable.

New technologies for the conversion of used edible oils and waste animal fats into biofuels appropriate for use in the standard diesel engines have been developed using alkali, acid, and alkali/cosolvent catalysts. All these technologies need substrates derived from oils or waste fats that have well-defined physical and chemical properties. The presence of free fatty acids and water complicates biodiesel production and needs to be minimized. Variations in the chemical and physical properties of the substrate derived from the used oil after pretreatment with various adsorbents have been receiving particular attention.

Our studies have been focused on the application of used rapeseed oil with a low content of erucic acid. The material was obtained from a commercial fryer after frying chicken breasts and fish fillets at 170°C for 10.5 h, and then stored at ambient temperature for 60 days.

Carbon-based adsorbents (active carbon, AC; active carbon oxidized with perhydrol [hydrogen peroxide], OAC) and mineral adsorbent (magnesium silicate, MS) were used in this study. Their porous structure and surface nature were analyzed on the basis of low-temperature (77°K) nitrogen adsorption–desorption and water vapor adsorption (298°K). Use was made of the BET isotherm (named after Brunauer, Emmett, and Teller, who derived the equation when working at the Fixed Nitrogen Laboratory in Washington, D.C.) to determine the accessible pore surface of the adsorbent. The greatest surface area was found with AC, and the smallest with MS. These parameters are listed in Table 1.

The oil purification process was designed to remove degradation products formed during frying and heat treatment.

Table 1
Physicochemical properties of adsorbents

Parameter	AC	OAC	MS
BET surface area, S_{BET}, $m^2\ g^{-1}$	980	895	198
Volume of micropores, W_o, $cm^3\ g^{-1}$	0.42	0.39	—
Volume of mesopores, V_{me}, $cm^3\ g^{-1}$	0.20	0.17	0.40
Mesopore surface area, S_{me}, $m^2\ g^{-1}$	207	178	159
Micropore surface area, S_{mi}, $m^2\ g^{-1}$	660	573	—
Number of polar centers (from water isotherms), a_o, mmol g^{-1}	3.46	7.60	—

(INEEL) in Idaho Falls, are developing a solid catalyst that does not dissolve into the reaction mixture, allowing for a continuous production process and producing a purer glycerol by-product that requires no cleaning. The sale of the higher-grade glycerol would make the process more cost effective, allowing the biodiesel to sell for a price comparable to petroleum diesel.

"Economics is the tough part here in the United States," said Ginosar.

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University of Idaho's Vandal Trolley runs on 20% biodiesel made from vegetable oil produced by UI's biological and agricultural engineering department.

Boise, Idaho-based french-fry maker J.R. Simplot Co. supplied Ginosar and Fox with used frying oil in the late 1990s for an initial phase of their investigation. A Cooperative Research and Development Agreement (CRADA) with a private firm has recently been signed, allowing them to expand the research.

When the process is perfected on an industrial scale, we could see waste oil-to-biodiesel conversion plants springing up next to food processing plants everywhere as food manufacturers recycle their massive volumes of used fats and oils into fuel for their trucking fleets.

Supermarket benefits

In another Idaho-based research project, University of Idaho (Moscow) graduate student Sam Jones worked with Boise-based Albertson's supermarkets in 2001 to develop an environmentally friendly way to dispose of used cooking oil from its delicatessens. The country's fourth-largest supermarket chain generates thousands of gallons of used cooking oil every month producing the fried chicken sold in their delis. Jones' premise was that Albertson's could recycle the oil to power the small diesel engines used to cool the refrigerated trailers carrying groceries nationwide.

Working with UI professor of agricultural engineering Charles Peterson and engineering specialist Joe Thompson, Jones developed a system for the delis to collect, strain, and filter the oil. Then Jones and Thompson evaluated blends of up to 10% used fry oil mixed with petroleum diesel to determine performance powering a refrigerated trailer Albertson's provided.

Although this project ended with Jones' graduation, the department continues to fine-tune and modify Jones' research. Thompson said the refrigerated trailer Albertson's provided is still being used by the department, running on a blend of petroleum diesel and 10% Albertson's used fry oil. "It has about 15,000 hours on it and is still going strong," he noted.

And while the grocery retailer is not using the recycled frying oil to power its refrigerator trucks quite yet, Thompson said Albertson's is fueling in-store heaters with used frying oil from the delis. "It saves on heating costs, and saves them the disposal costs of the used oil," he said.

To evaluate the efficiency of the adsorbents in the removal of the degradation products and their impact on the physical and chemical properties of the recovered used oil, certain parameters were measured: density (□), viscosity (□), acid value (AV), iodine value (IV), peroxide value (PV), water content, and freezing point (FP). The results are summarized in Table 2.

The desired quality requirements for the raw materials to be used in particular technologies of transesterification of used oils and fats are summarized in Table 3.

As can be seen from Tables 2 and 3, AC, OAC, and MS all show promise regarding the desired property changes in the raw materials used for the transesterification reaction.

Table 2
Physicochemical properties of used oil after different adsorption treatments

Oil used and after treatment	Density □ (g/cm^3)	Viscosity □ (□$Pa \cdot s \cdot 10^2$)	*AV* (mg KOH/g)	*PV* (mmol O_2/kg)	*IV* (g I_2/100g)	Water content (wt%)	Freezing point (°C)
	0.920	0.120	10.7	1.7	107.3	5.1	12
AC	0.915	0.131	5.2	2.6	106.5	0.9	15
OAC	0.912	0.123	3.8	2.8	106.4	0.5	14
MS	0.917	0.146	2.4	5.3	106.6	0.4	19

Table 3
Requirements for various transesterification processes for biodiesel production

Requirements/ process	Alkaline catalyst	Acid catalyst	Alkaline/ cosolvent catalyst
Water, wt%	0.5	0.5	
FFA, wt%	3	5	<30
Polymers, wt%	2	3	1
Iodine value, IV	105		
Freezing point, °C	50	30	10

Water and FFA contents are increased significantly by oxidized AC and MS treatments. Polymers probably will be recovered mainly by AC adsorption. The adsorbents used did not change the IV and the FP of raw waste cooking oil.

Adsorptive treatment of raw material before the transesterification reaction might require the use of a mixture of adsorbents having different physicochemical properties. Pretreatment of waste frying oil using adsorption technology to remove water and FFA can provide a substrate that can undergo more efficient conversion to biodiesel in the subsequent transesterification process. A number of problems still remain to be explored to analyze the full effectiveness of this technology. Appropriate studies are being conducted.

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