COMPLETION REPORT

WILLIAM AND BARBARA LEONARD
UNIVERSITY TRANSPORTATION CENTER
SEED GRANT PROJECT
2007

ASSESSMENT & DEVELOPMENT OF BIODIESEL INSTRUCTIONAL TECHNIQUES

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ABSTRACT

In this work I have evaluated the effectiveness of biodiesel instructional demonstrations using different feedstock oils and at various scales. Quantification of the clarity and color contrast of biodiesel and glycerin products of the biodiesel chemical reaction using different types of vegetable oil was performed, with canola oil being selected as the best combination of contrast and cost-effectiveness. A laboratory exercise appropriate for upper-division undergraduate students and first-year graduate students has been developed. A short video was prepared, presenting industrial-scale biodiesel operations and intended for both student courses and general public education. This video is already posted on the Transportation Center web page.

PROJECT SIGNIFICANCE

Alternative fuel research is one of the California governor's initiatives, and a focus area of stewardship listed on the California State University, San Bernardino (CSUSB) Transportation Center Research Agenda. Biodiesel is an alternative fuel that reduces many vehicular emissions (e.g., carbon monoxide and particulate mater up to 50% decrease and sulfur up to 80% reduction, http://www.epa.gov/otaq/models/biodsl.htm), and may be produced from renewable resources. While much work has been done on the mechanics and chemistry of biodiesel production and emissions, little has been done in the Inland Empire to develop public awareness of this fuel option and evaluate the best methodologies for this type of educational work.

RESULTS OF STUDY, PART 1

The purpose of this portion of the study was the development of new and original video and still-photographs for use in future PowerPoint presentations, and lectures for student and general public education. For field trips to potentially hazardous industrial sites it is not practical to take large numbers of students. It is also expensive and time consuming to transport the students long distances.

It was originally proposed to take video and photographs of small-batch biodiesel production steps at CSUSB, and industrial-scale biodiesel operations at Yokayo Biofuels in Northern California. Despite a previous willingness to cooperate with academia (based upon initial contact with their staff), Yokayo Biofuels in Northern California refused final permission as another company who was concerned about proprietary methodologies purchased them.

Fortunately, Biotane Biofuels, located in Imperial, CA agreed to permit videotaping of their new 8 million gallon per year capacity biodiesel facility. Their chief engineer was generous in leading this tour, and providing much information about their operations. Despite initial concerns about the size of operation, it proved much easier to video and photograph this sprawling large operation.

The video has been edited and has been posted to the CSUSB Transportation Center web site, and is also included with this report.

In addition, high-resolution still-photos of the Biotane processing facility and student experiments have been included on a separate disk, for inclusion in future PowerPoint presentations for use by the Transportation Center staff and faculty (see Appendix A for thumbnails of these pictures). The suggested interaction with Dr. Ed Chang was not completed, as e-mail discussions with him revealed that his research was vastly different from my proposed work.

RESULTS OF STUDY, PART 2

The purpose of this portion of the study was to examine visual clarity and color contrast of separation during transesterification (biodiesel production) of various vegetable oil feedstocks. Often, the oil feedstock that is used for class demonstrations produces poorly contrasting dark-colored biodiesel and dark-colored glycerin layers. While students can distinguish the layers in this non-ideal separation upon close examination, this would be useless for demonstration purposes with the larger enrollment courses such as NSCI 320 (Energy) that may have well over 100 students. Other workers have successfully produced desirable high-contrast transesterification and biodiesel-glycerin separation, though their oil feedstock type is not documented (e.g., http://journeytoforever.org/biodiesel_make.html#biodnew).

The visual clarity and color contrast of separation during transesterification of ten (10) oil feedstocks including waste vegetable oil (from campus food services), corn oil, canola oil, peanut oil, sesame oil, grape seed oil, rice bran oil, safflower oil, walnut oil, and olive oil, were quantified using a Lovibond RT-100 colorimeter, to determine the optimal oil for visual demonstrations in large classroom settings (Table 1). Color measurements were performed upon raw oil, biodeisel product, and glycerin byproduct for each oil. Quantification of color with this device is common in the food oils industry.

One of the more useful measurements of color are the coordinates of the Hunter **L, a, b** color space [R.S. Hunter, abstract, *Journal of the Optical Society of America*, **38**:661 (1948); R.S. Hunter, abstract, *Journal of the Optical Society of America*, **38**:1094 (1948)] A modernization of this system produced the CIE 1976 (*L**, *a**, *b**) color space. In this system, *L** refers to luminosity, while *a** and *b** refer to the actual color coordinates (see figure 1).

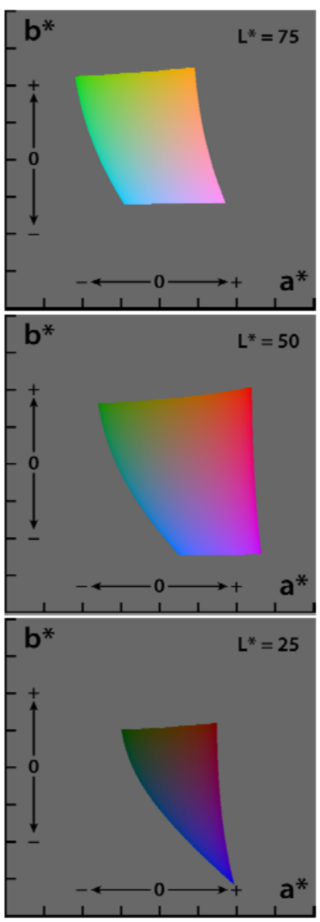


Figure 1. (source: Wikipedia)

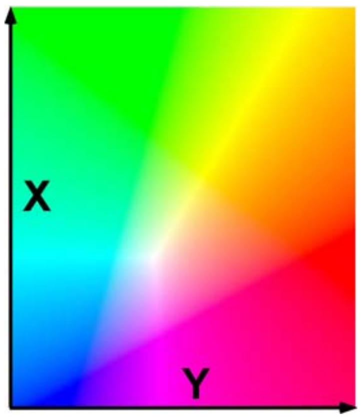


Figure 2. (source, author)

Another useful color space system is the CIE 1931 XYZ color space [CIE (1932). *Commission internationale de l'Eclairage proceedings, 1931*. Cambridge University Press, Cambridge; Smith, Thomas; Guild, John (1931-32). "The C.I.E. colorimetric standards and their use". *Transactions of the Optical Society* **33**: 73-134]. This is a similar, yet mathematically different system to *L* a* b** color space (see figure 2).

Yet a third system of color may be used for oils, biodiesel, and glycerin, especial in consideration of the general yellow color of most oils and whiteness of most glycerin. This third system uses the Yellowness Color Index (Yi), developed by the plastics industry for measuring fade and degradation of plastics in sunlight. This Yellowness Color Index may be compared to the samples Whiteness Index (Wi), a system developed by the ceramics industry to measure the purity of white porcelain.

The transesterifications were performed using accepted and standard procedures, using a titration-controlled KOH-Methanol reagent. Samples were not filtered or clarified with heat, to simulate field conditions in a classroom demonstration. Experiments were performed in the Stable Isotope Laboratory, a facility under the direction of the principal investigator. Replicate samples for some trials were produced by students in the GEOL 610 Environmental Geology graduate course as part of a laboratory exercise.

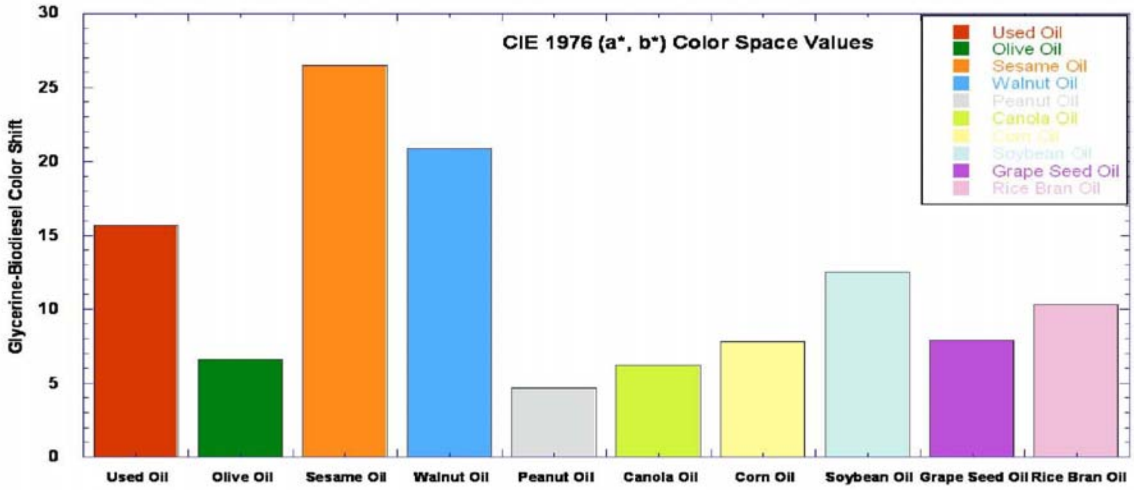
In any two-variable coordinate system, the difference between two points may be calculated using the expression: $\sqrt{(a_1-a_2)^2 + (b_1-b_2)^2}$

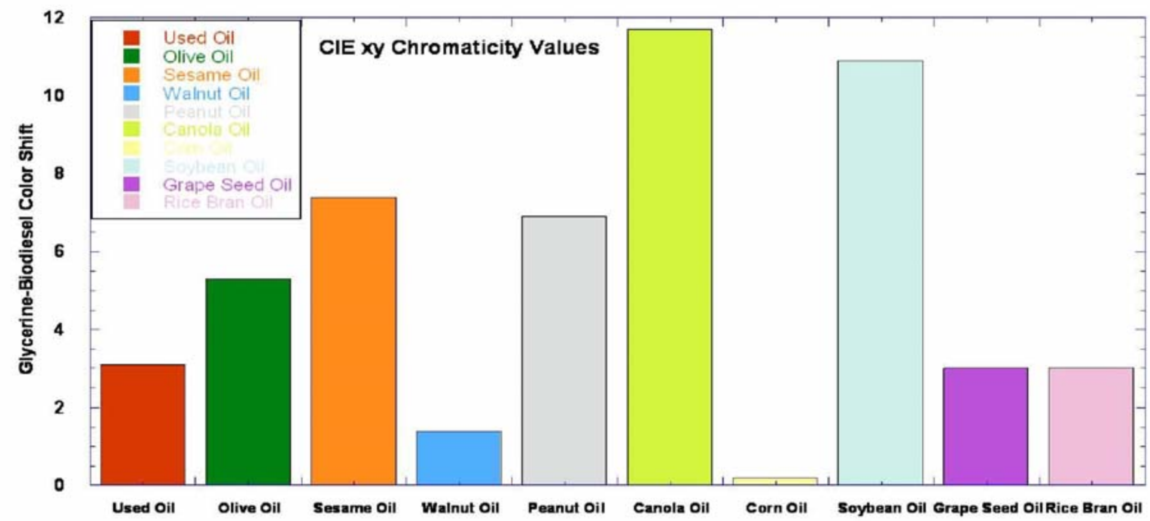
This calculation of color shift between glycerin and biodiesel for each color space was performed for all ten oil experiments (Table 1). Results of these calculations are presented in Figures 3, 4, and 5.

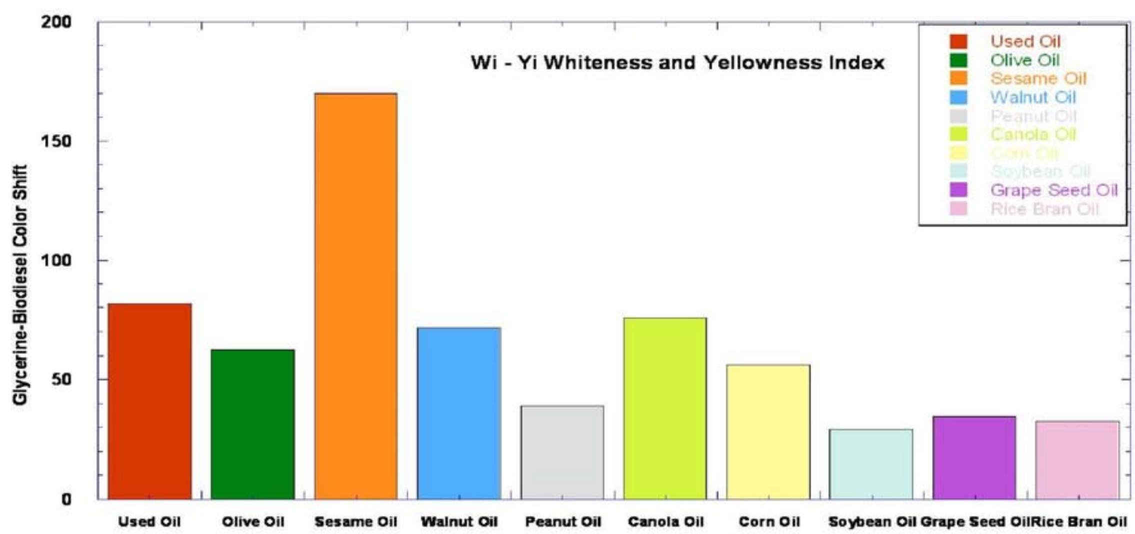
	canola oil	canola glycerine	canola biodiesel		corn oil	corn glycerine	corn biodiesel		soybean oil	soybean glycerine	soybean biodiesel		grapeseed oil	grapeseed glycerine	grapeseed biodiesel	
X	9.28	2.38	10.28	11.7	9.42	8	7.78	0.2	10.56	2.91	10.28	10.9	10.11	9.3	7.29	3.0
Y	10.11	2.46	11.08		9.81	8.66	8.57		11.41	3.03	11.08		11.3	10.49	8.29	
Z	3.61	0.62	4.4		3.17	1.93	2.86		4.81	1.44	4.4		3.54	2.28	2.38	
L*	38.03	17.72	39.71		37.5	35.32	35.15		40.26	20.16	39.71		40.07	38.7	34.59	
a*	-2.44	0.98	-1.69	6.2	0.94	-1.87	-3.17	7.8	-1.93	0.67	-1.69	12.5	-4.63	-5.22	-5.47	7.9
b*	28.63	21.52	27.08		30.43	36.12	28.43		25.98	14.82	27.08		32.53	38.95	31.05	
C*	28.74	21.55	27.13		30.44	36.17	28.61		26.05	14.83	27.13		32.86	39.3	31.52	
h*	94.88	87.39	93.57		88.22	92.96	96.37		94.25	87.42	93.57		98.09	97.63	99.99	
Wi	-246.28	-297.98	-225.47	75.7	-257.49	-313.93	-259.99	56.0	-214.71	-196.53	-225.47	29.3	-268.94	-321.07	-287.66	34.6
Yi	78.52	96.8	75.1		87.76	94.7	79.73		72.01	70.29	75.1		80.38	90.4	81.36	

	peanut oil	peanut glycerine	peanut biodiesel		walnut oil	walnut glycerine	walnut biodiesel		extra virgin olive oil	extra virgin olive glycerine	extra virgin olive biodiesel		sesame oil	sesame glycerine	sesame biodiesel	
X	5.92	2.32	6.97	6.9	10.75	8.32	6.95	1.4	6.81	2.93	6.31	5.3	1.48	0.4	5.62	7.4
Y	6.45	2.28	7.42		11.17	7.49	7.77		6.98	2.88	6.94		1.43	0.38	5.64	
Z	3.23	1.17	4.45		3.41	0.77	2.1		1.17	0.81	2.91		0.74	0.26	1.49	
L*	30.52	16.89	32.75		39.87	32.89	33.5		31.76	19.56	31.68		12.15	3.48	28.5	
a*	-2.09	3.36	-0.65	4.7	1.19	11.46	-4.06	20.9	1.96	3.72	-2.9	6.6	3.64	1.54	3.17	26.5
b*	18.02	12.38	14.81		33.01	45.52	31.48		37.98	21.92	22.11		10.14	2.26	28.69	
C*	18.14	12.83	14.82		33.03	46.94	31.74		38.03	22.24	22.3		10.77	2.74	28.87	
h*	96.61	74.82	92.5		87.94	75.87	97.35		87.04	80.37	97.47		70.24	55.8	83.69	
Wi	-186.39	-177.59	-144.18	39.0	-264.5	-348.07	-294.5	71.5	-336.5	-276.52	-221.86	62.4	-173.97	-120.63	-285.72	169.9
Yi	62.04	73.4	53.23		90.16	132.79	85.44		107.63	100.17	70.02		74.97	59.24	99.33	

	rice bran oil	rice bran glycerine	rice bran biodiesel		used oil	used oil glycerine	used oil biodiesel	
X	10.91	11.02	8.93	3.0	1.12	0.5	2.82	3.1
Y	11.29	12.09	9.96		1.06	0.31	2.42	
Z	2.3	1.34	1.73		0.62	0.34	1.04	
L*	40.06	41.36	37.77		11.42	3.81	17.57	
a*	1.57	-3.21	-4.22	10.3	3.64	1.24	10.12	15.7
b*	41.07	52.48	42.18		10.01	2.33	15.22	
C*	41.1	52.58	42.39		10.09	2.6	18.28	
h*	87.81	93.5	95.71		70.03	51.79	56.39	
Wi	-314.35	-375.27	-343.76	32.8	-155.25	-132.13	-198.48	81.8
Yi	102.33	105.87	96.79		76.76	53.77	101.68	







Figures 3, 4, and 5. Color contract shift between biodiesel and glycerin for all oil experiments.

Used oil (waste vegetable oil) was found to be of little use for demonstration purposes, as the opaque nature of both the resulting biodiesel and glycerin makes for poor display. There are also undesirable health issues related to the storage and handling of waste vegetable oil.

Sesame oil was found to produce a similarly opaque biodiesel and glycerin. This oil produced the most uniformly sharp color contrast, but this was only observed at close range or when highlighted by lighting through an overhead projector unit.

Olive, corn. rice bran, and grape seed oils were also found to be undesirable, for the opposite reason. In these cases, the products were beautifully translucent, but with little color contrast.

Peanut oil produced excellent color contrast, but was found to be difficult for complete transesterification and often produced an emulsion. This instability makes it undesirable for on-the-spot classroom demonstrations.

Walnut oil also produced excellent color contrast, but is prohibitively expensive for classroom use and difficult to find at most stores.

Canola and soybean oils have excellent color contrast, are translucent, are inexpensive, and widely available. Of these two, canola oil has a marginally better contrast, with soybean coming in a close second. Both oils are recommended for demonstration purposes.

Lastly, a complete laboratory exercise has been generated for future student use (see Appendix B). This laboratory exercise has been adapted, with permission, from the director of the biodiesel research group at http://journeytoforever.org/biodiesel.html.

APPENDIX A

BIODIESEL PHOTOGRAPHS

GEOL 610 Biodiesel Laboratory

GEOL 610 Biodiesel Laboratory

GEOL 610 Biodiesel Laboratory

Results of all biodiesel experiments

Biotane biodiesel storage

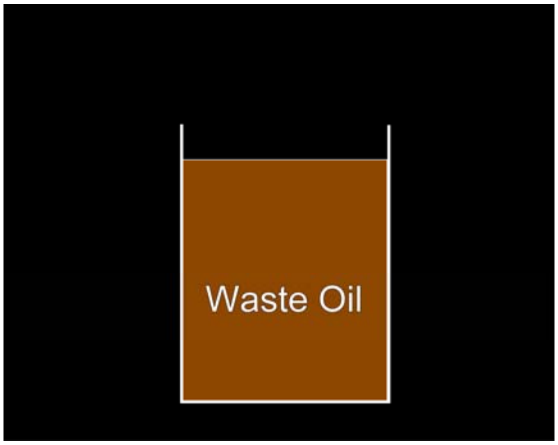
Biotane biodiesel storage

Biotane waste oil storage

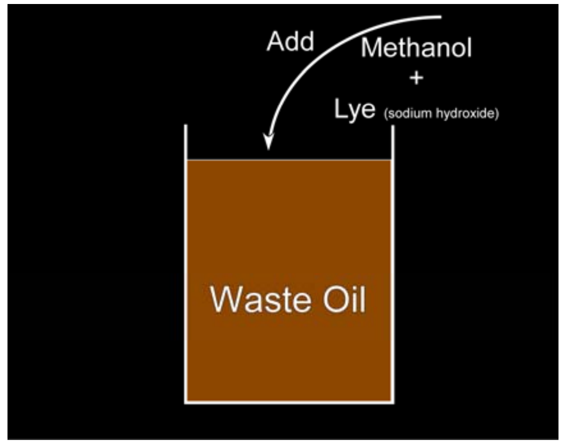
Biotane plant, Imperial, CA

Sunline hydrogen fueling station, Palm Springs, CA

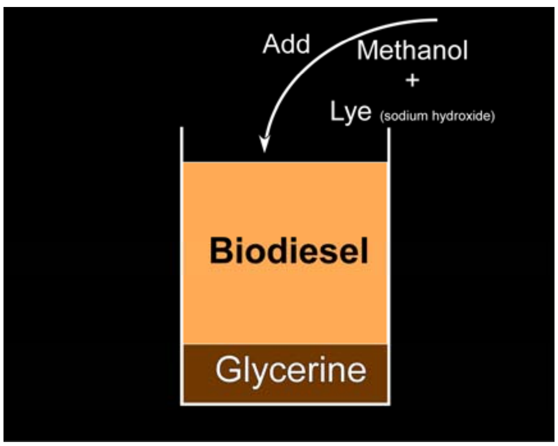
Sunline hydrogen fueling station, Palm Springs, CA



Biodiesel production slide 1



Biodiesel production slide 2



Biodiesel production slide 3


Palm Springs wind farm


Pearson Fuels biodiesel pumps
San Diego, CA

Pearson Fuels biodiesel, natural gas and ethanol pumps

Pearson Fuels biodiesel and E85 pumps

Examples of biodiesel, Biotane

Biotane, fish oil biodiesel

Palm oil biodiesel, showing problems with saturated fat “soaps”

APPENDIX B

BIODIESEL LABORATORY EXERCISE

Bio-diesel from waste vegetable oil

(As liberally adapted and modified, with permission, from http://journeytoforever.org/biodiesel.html)

Supplies:

- Magnetic stir/hot plate or blender and hot plate
- Thermometer
- 1 2L Flask
- 1 1.5L Beaker
- 1 funnel
- Measuring beakers or graduated cylinders
- Balance accurate to 0.1 gram or less

Reagents:

- 1 liter of vegetable oil
- 200 ml of methanol, 99+% pure
- Lye catalyst -- either potassium hydroxide (KOH) or sodium hydroxide (NaOH)

STEP 1. The reaction process

1). Pre-heat the oil to 55 deg C (130 deg F) in a 2 liter flask. Drop in a magnetic stir bar.

2). With the stir plate and hot plate switched **off**, carefully pour the prepared methoxide from the HDPE container into the oil.

3). Cover the flask tightly and switch the stir plate on. Medium speed should be enough. Mix for 15 minutes.

4). Continue mixing as above, but turn on the hot plate and maintain temperature at 55 deg C (130 deg F), process for 45 minutes.

STEP 2. Transfer and Settling

Freshly made biodiesel, 20 minutes after processing

After the reaction process above, use a funnel and pour the mixture into a 2-liter PET bottle for settling and screw the lid on tightly. As the mixture cools it will contract and you might have to let some more air into the bottle later. You may also cover the top of the flask with parafilm for cooling and settling. Allow settling for 12-24 hours.

Darker-colored glycerin will collect in a distinct layer at the bottom of the bottle, with a clear line of separation from the pale biodiesel liquid above. The biodiesel varies a little in color, according to the oil used (and so does the by-product layer at the bottom) but usually it's pale and yellowish, while used-oil biodiesel may be darker and more amber. The biodiesel might be clear or it might still be cloudy, which is not a problem. It will clear eventually but there's no need to wait.

Carefully decant the top layer of biodiesel into a clean jar or PET bottle, taking care not to get any of the glycerine layer mixed up with the biodiesel. If you do, re-settle and try again.

STEP 3. QUALITY TESTING

The wash test is the most useful all-round test, and it's very simple: Put 150 ml of unwashed biodiesel (settled for 12 hours or more, with the glycerine layer removed) in a half-litre glass jar or 1-liter PET bottle. Add 150 ml of water, screw the lid on tight and shake it up and down violently for 10 seconds or more. Then let it settle. The biodiesel should separate from the water in half an hour or less, with amber biodiesel on top and milky water below. This is quality fuel, a completed product with minimal contaminants. Wash it, dry it and use it with confidence.

Wash-test with unwashed biodiesel -- left, after a violent 10-second shaking; right, biodiesel and water separated cleanly within minutes. The biodiesel will be cloudy, and the water can be milkier than this, but as long as it separates quickly and cleanly, it passes the test.

If it turns into something that looks like mayonnaise and won't separate, or if it only separates very slowly, with a creamy white layer sandwiched between water and biodiesel, it's not quality fuel and your process needs improvement. Either you've used too much catalyst and made soap, or a poor conversion has left you with half-processed mono- and diglycerides, fuel contaminants that act as emulsifiers (better titration, try more methanol, better agitation, longer processing time, better temperature control), or both too much catalyst and poor conversion.

Whichever, you're headed for washing problems. Super-gentle washing techniques might avoid the problems, but you'll still be left with poor-quality fuel laced with contaminants.

If you have an emulsion any thicker than the normal "paper thin" interface layer between oil and water, the batch should be retreated. Retreat as with fresh oil, with the standard 3.5 g of lye per liter of oil but using only 100 ml methanol per liter of oil.

Bubble-washing is also gentle, and it's worth repeating the test with some washed fuel after bubble-washing -- it should separate from the water cleanly within a few minutes.

Color and Quality

- Nicely cracked biodiesel: very pale yellow (less than virgin sunflower oil) and no change in color with artificial lighting;
- Acceptable biodiesel: yellow like virgin sunflower oil or straw, but will get orangey undertone in reflected tungsten light;
- Deeper color biodiesel has a lot of glycerine in it in the form of various glycerids. Not good for standard engines. Remedy: If the diesel is too dark and you are sure that you used the correct quantitie(s) of catalyst(s), add a pinch more alcohol -- you could be losing it due to evaporation."

THE PROCESS

Vegetable oils and animal fats are triglycerides, containing glycerin. The biodiesel process turns the oils and fats into esters, separating out the glycerin. The glycerin sinks to the bottom and the biodiesel floats on top and can be syphoned off.

The process is called transesterification, which substitutes alcohol for the glycerin in a chemical reaction, using lye as a catalyst.

STEP 4. Stir Washing

Stir-washing a 60-litre batch -- in goes the first wash water, 20 litres of it.

A paint-stirrer on a drill agitates the whole tank (avoid making a vortex, but it helps for photographs!).

The double paint-stirrer. Three washes in a day leaves the biodiesel clean and clear, with no emulsion formed and no loss of yield.

1) Make absolutely sure that you never try to wash an incomplete reaction by test-washing a 1-ounce sample in a sealed jar.
2) Use a motor-driven impeller to mix the water/fuel mixture to the point of appearing homogenous for about 5 minutes.
3) Let settle 1 hour.
4) Siphon off the top layer of fuel and repeat steps 2, 3 and 4 two more cycles.
5) Let the fuel air-dry or heat to 120 deg F (48 deg C) to dry.

Depending upon the volume of oil in your batch, the hp/size of your reactor tank and wash tank motors/impellers, you could get your entire batch process time down to 24 hours.

Advantages of stir-washing: Quick and effective, no masking of a poor reaction, no oxidation.

Disadvantages of stir-washing: There aren't any. BUT you have to process the fuel properly in the first place. Some beginners have difficulty with this, all seems well until they start the wash, and hit problems -- it foams, or it turns into chicken soup and won't separate. And then they get discouraged. Don't get discouraged and keep trying! It's just a matter of practice and getting a good feel for the biodiesel process. Make sure your titration and measurements are accurate, be as meticulous as you can, make sure your chemicals are fresh and high-quality, that you're using enough methanol, that you're processing the fuel at the right temperature and agitating it for long enough.

STEP 5. Drying the fuel

When the fuel is clear -- not colorless but translucent, you can see through it, there's no haze or cloudiness -- then it's dry. Actually it's never dry: despite what the standards say, it always absorbs some water from the atmosphere, between 1,200 and 1,500 ppm, but this is dissolved water, which is harmless, unlike suspended water.It should clear by itself in anything from a day or so after you separate the final batch of wash-water. Leaving it in the sun will help, or heat it to 45-50 deg C (113-122 deg F) and let it cool in a vented container. If it goes cloudy again on cooling you probably haven't washed it thoroughly enough. Give it another wash. If you're in a hurry, heating it to 45-50 deg C a second time might clear it. If it doesn't clear, it probably needs reprocessing.