

## “I don't have money to burn, but I have lots of glycerin...”

Olen Soifer, 05-15-2007

### Introduction

In the world of alternative, bio-fuels, there are various major hurdles to overcome and “equations” to consider. If the hurdles are not surmounted, then the entire venture to replace petroleum fuels with “green” energy sources is an interesting, but unnecessary, undertaking...at least until petroleum fuel sources are depleted. The most important and substantive challenges of biofuel production include:

- 1 **The Energy Equation:** That is, the energy efficiency of the entire series of processes used to produce the fuels versus the energy contained in the fuel produced. This energy cost includes:
  - 1.1 the cost to growing the oil-bearing raw materials;
  - 1.2 the energy used in manufacturing the product;
  - 1.3 the costs of transportation of the product to the end user;
  - 1.4 the costs to handle, transport &/or dispose of wastes produced.
- 2 **The “Green House Gas (Carbon) Equation:** That is, the amount of carbon that is released to the atmosphere when the fuel is produced and ultimately burned compared to the amount of carbon derived from the atmosphere. This must include carbon that had been bound for many years (in petroleum, methane, old growth tropical forests, etc) which is released in the crop growth, production & transportation of the product;
- 3 **The Raw Material/Product/Recycling/Waste Equation:** That is, the efficiency of process in terms of the fuel yield compared to the amount of raw materials used, compared to the amount of product produced, as well as the recapture and recycling of wastes/byproducts with minimal environmental impact from the entire process versus the production of totally valueless waste;
- 4 **The Community/World Equation:** That is, how much “green” impact the process has on the community in an environmental, as well as economic, sense. Controlling this equation requires a conscious, sensitivity toward the global, as well as local, impacts of the venture. Major considerations include:
  - 4.1 the inevitable increase in food and feed costs as agricultural products are diverted from food/feed to fuel production
  - 4.2 the environmental impacts of the production which may be beneficial in one area (ie: reduced local emissions) but detrimental in other areas. Deforestation to increase crop land is a particular problem:
    - 4.2.1 it increases greenhouse gases because the cut forests are always burned
    - 4.2.2 it provides additional land for crops but the land is of low fertility (requiring petroleum-based fertilizers after a short time) and is subject to extreme erosion
    - 4.2.3 the crops that are grown, instead of trees, do not replenish the atmosphere as well as the original, vanished forests
    - 4.2.4 animal and plant species become extinct...with ethical, biomedical and other ramifications.
  - 4.3 the inevitable trampling of local/indigent persons rights and economic status when corporate giants begin to dominate the biofuel industry...this includes increased fuel costs &/or fuel unavailability to those same local populations. Unfortunately, very little economic benefits “trickle down” to the local populations.
- 5 **Economic Factors:** Primarily, the problem is one of the cost to produce the fuels in economic competition with “normal” fuels derived from petroleum. The products must be competitive without artificial subsidies, even if those subsidies are used to initially “kick-start” production.

**In this paper, the focus is on the major byproduct of biodiesel production...dirty glycerin. But each of the other challenges are touched upon. Inexorably, they are all linked to each other.**

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How many biodiesel (or potential) producers have ever stopped to consider what they are going to do with all of the waste glycerin that is generated from biodiesel production? Even though the glycerin it is not toxic, if the lye in it is removed or neutralized, too much of good thing is still not so good! For most people, milk is nontoxic also. But that doesn't mean they can't drown in enough of it!

Purified, or mostly purified, glycerin should be worth money. But it must be in the area of 95% pure, while biodiesel “goo” is about 80-85% and accompanied by a lot of, pardon me, “crap” Some of the “byproducts in the byproduct” are not safe. Manufacturers will only pay a few pennies a pound for our crude glycerin, if they take it at all. Many producers will actually have to pay someone to take the stuff away. It's already happening. More quickly than anyone anticipated, the byproduct went from a being considered a raw, glycerin resource, to a glut of waste.

Even if producers consider distilling the stuff, it must be remembered that distilling glycerin requires temperatures about a hundred degrees above the boiling point of water. At that temperature, it becomes a fire and explosion hazard. The distillation process contradicts one of the nice things about making biodiesel, which is that it rarely involves temperatures much higher than that of a hot bath. Distilling glycerin is another matter and a process not to be taken lightly.

Large biodiesel processors are being forced to deal with their byproduct because of the sheer volume of it they are becoming saddled with. They don't have the luxury of a home producer, who can let the stuff collect up in some drums until he figures out what to do with it. On the other hand, the large producer should have the capital to buy the technology that can turn the raw byproduct into a pure, valuable, commodity. The small processor doesn't have that luxury.

Because of the nature of the business, it is hoped that large processors will accept raw glycerin byproduct from small processors, even if they don't pay for it. It would be politically and environmentally “correct”...a way of showing that there is more to the biodiesel business than saving or making money. Such a policy could not be considered “helping the competition”, because a fellow who “brews up” a few hundred gallons of biodiesel, per year, doesn't present serious competition to a company that processes 50,000 gallons a week.

What do we do with all of this waste glycerin? There is a lot of talk about how good the byproduct is as a degreaser. Some processors have found mechanics to take the stuff off their hands, or even buy it. But there are only so many dirty mechanic's hands to be washed, and engines to be degreased, and the amount of the stuff generated is no small matter.

Even if the stuff can be turned into a good degreaser, the byproduct we end up with can not be considered to be glycerin soap. It is glycerin, with a little soap in it...along with lye, some unremoved biodiesel, unprocessed, free fatty acids and oil and other matter. Making it into real glycerin soap requires the addition of more lye, at about 5 times the ratio of lye to oil in the original biodiesel “recipe”, plus a lot of cleaning and processing. Most of processors won't waste their time or money doing to create a product that is not competitive with glycerin soap made conventionally!

For good or bad, soap is far less valuable than fuel, especially considering the quality and appearance, of the final product. The liquid glycerin cleaning product that a small producer can make, and even the real glycerin soap they can produce, will probably not appeal to buyers of “fine glycerin soap”. If you doubt that, buy a small bottle of pure glycerin, and a bar of glycerin soap, at the drug store. Compare these clear, almost glass-like items to your “degreaser goo” or the chocolate colored glycerin bar you can make. No-one would possibly confuse one with the other! It is a reality that most people could not be convinced to choose the dirty looking product over the one from the store. Trying to convince people that buying it is a step toward saving the planet will be as successful as

trying to convince them to eat a bug in their soup because it contains more high quality protein than lean beef.

Did a “light-bulb go off in your head”, to the effect that glycerin might, itself, make a good fuel because heating it is a fire hazard? .Can't we really burn glycerin? If you thought that, you are not the first one to think of that...because glycerin does burn. But those who are trying to burn it, have come up with some interesting results. Mainly, they have learned that the byproduct has a tendency to “glop up” most burners with coke and soot. (Residual soaps and all that...)

The bigger problem is that glycerin doesn't burn all that well in a home furnace. It also produces toxic acrolein if burned at much less than 1,000 degrees...a temperature no reached in that home furnace. The trade off for heating your house for nothing could be that you kill yourself, and/or your family, from the fumes.

There are burners that can safely, efficiently and cleanly burn glycerin, as a fuel, but they burn it at those higher temperatures that a home furnace does not attain. They are more complicated, and more expensive, than practical for home use. There are some companies that are working on this problem, but there is no reliable, affordable home burner, that I know of, which can presently handle the stuff right now.

Does one plus one plus one equal two? Some biodiesel environmentalist would have us believe that. It comes for another problem that burning glycerin raises and which we must consider: Most people realize that the increasing manufacture of biodiesel is taxing the ability of the world to supply adequate quantities of vegetable oil raw material. Those demands for raw oil for biodiesel are resulting in mass clearing and burning of rain forests in Malaysia and Indonesia for use in growing the Oil Palm...along with the destruction of Amazon rain-forest to grow sugar cane for ethanol. Creating biofuels to cut the production of green-house gases sounds noble, at first, but the destroyed rain forests are always burned and that is releasing enormous amounts of CO<sub>2</sub>...which the use of biofuels was expected minimize.

The result is that the highly touted “carbon neutral” advantage of biodiesel is defeated. If you will recall, burning a “carbon neutral” fuel means that the carbon produced by burning it merely replaces the carbon removed from the atmosphere by the organism that created it.

“Ahhhh!”, you say, “I am only using waste oils or oils that do not come from plants grown on burned rain forests...and the biodiesel produced prevents the release of ”greenhouse” gases from the same amount of petroleum I didn't have to burn”. That sounds logical, but there is a problem: Methanol can be made by the “green” method of “destructive distillation” of wood. (“Green, that is, if the wood is grown specifically to produce methanol...”) Unfortunately, most of it is made from natural gas, methane, because huge resources of the gas have been discovered in places like Trinidad. Liquid petroleum and gaseous methane should both be considered to be petroleum. When either is burned, it releases carbon gases to the atmosphere which have been chemically bound up in the earth for thousands of years.

It may be true that you don't specifically don't burn when you make biodiesel. But, isn't it a matter of semantics when methanol molecules are added to a fatty acid (oil molecule fragment), to make biodiesel and the biodiesel is burned? I suppose someone has to do the chemical math and energy equation by comparing the burning of the original triglyceride oils versus burning the methyl ester biodiesel. It is probably not much of a difference.

Another part of the equation has to be considered if the glycerin were also burned. In that case there would be a net carbon increase in the atmosphere unless the alcohol used to create the biodiesel was “green”, as opposed to being petroleum or natural gas derived. In that case, the net result is that the carbon which the plant pulled out of the atmosphere, originally, would be released along with the carbon from the methane (source of the methanol) used to produce the biodiesel.

If biodiesel was only made from ethanol, that would take the carbon from methane out of the equation and replace it with carbon that the source grain plant pulled out of the atmosphere. It sounds great at first, until we consider that much ethanol is made from corn. And corn depletes soil, requires lots of tending, plus pesticides and fertilizers that are made from ( you guessed it...) petroleum. We can hope at least, that biodiesel is used to power the machinery tends and processes the corn!. If we can get the price of the stuff down, and use a source grain that

doesn't have the problems associated with corn, we might "get a handle" on this carbon problem. But, for now, ethanol more expensive than methanol. It is too expensive for a lot of biodiesel producers and methanol remains in the process.

This issue is similar to the problems inherent with electric cars. They sound like a panacea because the driver doesn't burn put carbon into the air in order to get it to move. Or does he? Where did the electricity come from to charge the thing? One would hope it was generated by a hydroelectric plant. But it is more likely that it came from a power plant that burns thousands of tons of coal to run it's generators.

It is like overlooking the problem of palm oil being produced for biodiesel. That is, oil extracted from plants grown on burnt over rain forests in places like Malaysia. These are problems that are overlooked when we don't "look beyond the end of the nose on our face". Unfortunately, while we are congratulating ourselves for our environmental consciousness, we are not "connecting the dots" that should point out that solving one problem in one place might have created a related problem elsewhere.

Consider that you will be neutralizing your glycerin to get rid of the lye in it. The cheapest way to do that is with muriatic (hydrochloric) acid. Unfortunately, the acid (HCl) combined with the lye (NaOH) makes water and salt. What do you do with this dirty salt? You may have a fair amount of it. A solution is to use ethyl alcohol and "potassium" lye (AKA "caustic potash", KOH) and then neutralize the end product with phosphoric acid. You end up with a lovely potassium phosphate fertilizer. (Of course, you don't want to get it in lakes and streams).

You also eliminate poisonous methanol with drinking alcohol and phosphoric acid will likely be a bit weaker than hydrochloric.

The problems are: Ethyl alcohol is harder to get dry enough (1% max water) to prevent making soap instead of biodiesel...but it can be done. Also, it is more expensive than methanol. You can use KOH and methanol, but it is harder to dissolve than in ethanol (or lye in methanol).

We must also keep the dirty secrets of biodiesel in mind: Methanol is made from natural gas...and we are trying to avoid use of hydrocarbons from the ground by making biofuels. But, if the origin of the oils is an important consideration: Remember that imported palm oils (good yield per acre) may, very likely, come from palms grown mostly in Malaysia and Indonesia...on former rain forest land. If you use corn oil, remember that it is an extremely soil depleting crop, requires lots of pesticides, and is very low yield in terms of oil. If you use soy oil that is imported by ADM, consider that they are being investigated for encouraging (or, at best, overlooking) the abuse of other carbon-containing units...that is, the people that make up the slave labor involved in the soy oil's foreign production!

This may be "raining on a parade"...but we really need to consider what are we going to do with all of this crude glycerin. Even after all of our engines are sparkling clean; our mechanics "smell like roses"; we have composted as much glycerin as possible; and added as much of it to animal feed as the animals will tolerate...we are still looking at the possibility of being overwhelmed with the goo!

It's a sizable problem and hopefully one that many amateur and professional "biodiesel chemists" keep working on. But, there are hopes for the future. For example, Dr. Galen Suppes, U. of Missouri, developed a catalyst to convert glycerin to propylene glycol more inexpensively than from petroleum. 2.6 billion pounds is made from petroleum each year, compared to the smaller need for glycerin. PG is an antifreeze, etc; is less poisonous than ethylene glycol, is worth \$ 1.50 per pound, or more, and can be made for 40(?) cents per pound from glycerin. Acetol, which can be converted to propylene glycol & various plastics, costs 50 cents a pound to make from glycerin, but \$5.00 a pound from petroleum.

A strain of E. Coli can turn glycerin to ethanol; and other techniques are being designed to produce much more valuable organics from the cheap glycerin waste...so, there is hope for the future that we will not have too much of a good thing.