Treatment, Disposal and Reuse of Biodiesel Derived Waste Products

By: Greg Austic, Piedmont Biofuels and Simon Lobdell, Chatham Environmental Consulting

Contact Information:
Greg Austic - greg@biofuels.coop
Simon Lobdell - Simon@chathamenv.com

Executive Summary

Wash water derived from the manufacture of biodiesel are difficult to treat through traditional methods. The water contains significant concentrations of carbonaceous material that must be treated before the wash water is released back into the environment. The following white paper presents several important points to consider when deciding how to dispose of wash water from the biodiesel production process. A case study is presented in which a variety of production methods and feedstocks are used to produce biodiesel. We then consider how those factors impact wash water quality, and how a wastewater treatment plant may consider treating different types of biodiesel wash water.

Background

High strength industrial wastewater is a problem in many industries including food processing, chemical manufacturing and refining. Biodiesel waste water has many of the same difficulties as the aforementioned sectors. While water washing in biodiesel is avoidable through the use of magnesol and ion exchange resins, water washing is sometimes a more convenient method of removing contaminants from crude biodiesel. Ion exchange resins can be clogged or quickly deactivated with high levels of soaps and do not remove many trace water-soluble compounds. Magnesol is another good option; however, it has associated disposal costs and can be difficult to remove without expensive equipment that is affordable only to larger producers.

Many industries have their own on-site wastewater pre-treatment or full treatment plants and indeed large biodiesel production facilities should consider this as a primary option. However, the plant should be prepared for a lengthy and complex permitting and design process especially if there is no local Publicly Owned Treatment Works (POTWs) to whom they may discharge the treated water. The most appropriate treatment and cost effective disposal methods for wash water have not been well applied in the nascent biofuels industry. Many biodiesel plants have been fined or even shut down as a result of discharging very high strength effluent to local POTWs. As a result, some biodiesel plants pump and haul their wash water to composters and other commercial waste treatment sites, which adds significant cost and is generally an inefficient and cumbersome addition to the plant's daily activities.

If possible, discharging wash water to a treatment facility is the best, easiest, and cheapest disposal method. However, the wash water must pass the quality standards of the treatment plant. While every treatment plant has their own standards, discharging any significant quantity of crude wash water will almost certainly be unacceptable. There are some scenarios under which the POTW may consider accepting a biodiesel plant's wash water: increased discharge rates, the POTW has significant excess capacity, the town wants to incentivize the business to build the plant, or possibly because the town is simply unaware of the levels of carbonaceous material in the waste water.

From an industry perspective the most difficult option is for the sewer authority to require the plant to meet municipal sewer standards. These are very restrictive and the plant will almost surely need an aggressive pretreatment plant including physical, chemical, and biological treatment steps. The second option is that the POTW will accept a certain volume of waste be discharged to the plant at higher strengths but will assess a surcharge for the extra treatment costs associated with the waste volume. Finally, some plants are not limited by the mass of carbonaceous and oxygen demanding materials entering their system and will take the wastewater stream without serious complaint. These plants are usually referred to as operating in a hydraulically limited state. In this case, operators and local authorities may allow discharge of higher strength wastewater on a restricted schedule but without any surcharge. Ultimate authority to grant a discharge permit to the biodiesel plant lies with the POTW. Any significant industrial operation must get explicit permission to discharge any of their process related wastewater into the public sewer.

Characterizing Wastewater For Discharge

Biodiesel wash water has extremely high biochemical oxygen demand (BOD), total dissolved solids (TDS), glycerin and residual fats, oils and greases (FOG), as well as highly acidic and basic conditions based on the generating process. Untreated wash water has been found to have concentrations in excess of 75,000 ppm BOD and very high concentrations of FOG with a very basic pH. The components which most greatly affect the critical parameters of wash water are: fatty acids (usually in the form of soaps), biodiesel, methanol, free glycerin, and minor components in the oil (crude soy gums, for example). These parameters are directly determined by feedstock type and method of processing and can vary greatly both plant to plant and batch to batch. The removal of these materials is key to achieving quality specifications acceptable for most waste water treatment plants.

The standard activated sludge basin used to treat wastewater from municipal sources is designed to handle wastewater with approximately 250 ppm BOD and less than 100 ppm FOG. When significant volumes of high strength wash water enter the system at inopportune times, the plant can be overwhelmed and not achieve the necessary treatment to be acceptable for discharge. As an example, a thousand gallons of 10,000 ppm BOD biodiesel wash water is equivalent to discharging 40,000 gallons of water at the normal 250ppm BOD limit from the perspective of the POTW. For a small municipality, this BOD load can represent a tremendous operational hurdle.

There are several concerns for the sewer authority. First and foremost, the presence of high concentrations of oil and grease may coat the sewer pipes and submersed motors leading to excessive maintenance costs and premature mechanical failure. The pH of wash water should never be outside of the range of 5 to 9 if it is to enter any sewer system. This is to protect the pipes, manholes and other physical infrastructure of a sewer system as well as the waste treatment process. Finally, if a high proportion of the water treatment plant's influent is from a biodiesel processor or there are plant specific concerns regarding salts, the high TDS associated with biodiesel wash water may lead to inhibition of the plant's bacterial activity and thus reduced treatment efficiency.

Therefore, it is critical to establish the expected criteria including volume, waste strength, discharge schedule and control strategies in conjunction with the sewer authority to ensure smooth plant operation on both sides. It is a reasonable outcome that the plant may ask the discharger to pay a surcharge of between 15 and 30 cents per lb of excess BOD discharged. However it must be stressed that this is at the plant's discretion and they have *no obligation* to accept wash water that exceeds their criteria.

Pretreatment and Appropriate Handling

Biodiesel operations handle a wide variety of liquids including glycerin, wet methanol, acidic methanol, and others. Keeping these waste sidestreams separate is important to the plant's ability to properly manage them. The only material that is likely to be acceptable for direct discharge is pretreated water. Water from the biodiesel washing process should be directed to a pretreatment step to remove the bulk of the contaminants and from here transferred into a single clean tank devoted to handling wash water. Further biological treatment to reduce the concentration of carbonaceous material is also an option. Unfortunately, many small to medium producers have not considered even the basic treatment described above. Furthermore, even with treatment, the critical design element is to understand what quality of waste water the local POTW will accept and designing a process to achieve this specification.

Designs to achieve the POTW requirements will almost always require some changes or additions to the process. Modifying the biodiesel production process to reduce the presence of carbonaceous materials in the waste water stream should be considered before extensive new waste water treatment options. are explored. The most important single step a biodiesel plant can make to reduce its waste water strength is the introduction of methanol recovery from its biodiesel before any washing takes place. As described in the case study below, methanol makes up the majority of the BOD in the wash water - therefore, removing methanol before washing will solve a large part of the problem. Minimizing washing through the use of ion-exchange resins or filter aids to reduce the number of washes will also decrease the quantity of wash water produced. These two basic steps, in addition to the waste water pretreatment described below, will go a long way towards achieving achieving a waste water acceptable to most POTWs.

Case Study - Pretreatment

One common method of treating biodiesel wash water is through physical-chemical separation. Some larger industries may consider continuous flow systems such as chemical coagulation and Dissolved Air Flotation (DAF) systems. However, a simple batch style system can be attractive for small to medium producers.

Piedmont Biofuels Industrial has been treating its wash water with acid to neutralize the soaps and release the free fatty acids and entrained biodiesel from emulsion. The system is essentially passive and the recoverable product floats to the top of the wash water processing tank. A pH of 3.5 or less must be achieved for full separation of the high acid biodiesel layer and water layer. While heat can improve the settling process' speed and effectiveness, the separation will form even at low temperatures. Because production process changes can drastically impact the quality of the water, the top phase (consisting of high acid biodiesel) phase has measured between 5 – 32% of the total quantity of wash water depending on feedstock type, catalyst type, washing time, heat during washing, and other factors. Recovering this carbon rich layer greatly improves the quality of the water from the standpoint of the treatment facility, and provides a stream of free fatty acids and biodiesel which can be reprocessed using acid esterification, or burned in a boiler built to handle fuels with higher acidity. Most of the free mineral acid, in this case HCl, ends up in the water layer. Piedmont has been using this method to recover lost product for nine months and has processed approximately 80,000 gallons of wash water in total and recovered around 10,000 gallons of high free fatty acid biodiesel.

Recently, continuous methanol recovery has been performed on the crude biodiesel at Piedmont Biofuels. Understanding the effectiveness of the methanol removal and its impact on wash water quality is critical to Piedmont's ability to discharge to the local waste treatment plant. Other important factors to understand are the fatty acid level of the transesterified feedstock and the type of feedstock.

Experimental Method

Three different samples of crude biodiesel were acquired. Each sample is described in the table below. All samples were kept in sealed containers after sampling to ensure no methanol evaporation.

Oil sample #	sample location	% FFA feedstock	% FFA feedstock (after acid esterification)	process description
1	Piedmont Biofuels Cooperative	4.08%		Transesterified from used vegetable oil. settled 18 hours before sampling, 8g/L base catalyst amount
2	Piedmont Biofuels Industrial	0.94%		Transesterified from crude soybean oil, settled 3 days before sampling, 8g/L base catalyst amount
3	Piedmont Biofuels Industrial	10.40%	0.41%	Acid esterified and transesterified from used canola oil, settled overnight. 7g/L base catalyst amount

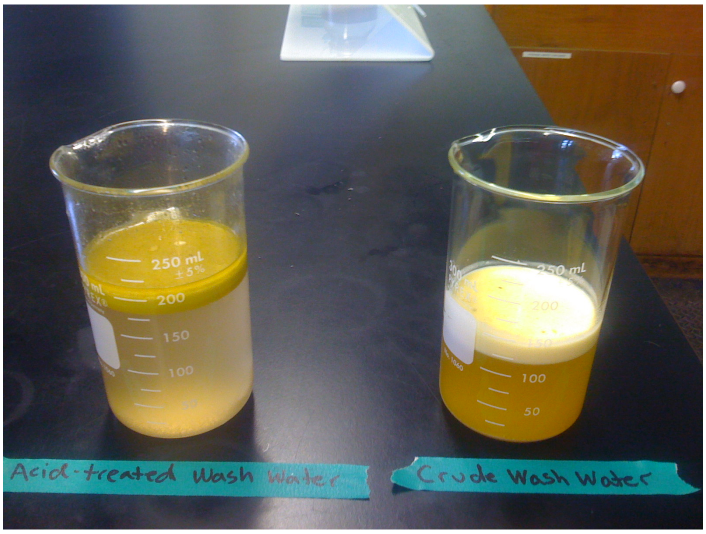
Table 1: Oil Sample Data

Each sample was split into two batches; one batch had the methanol removed, the other did not. Methanol recovery was simulated in the lab under a fume hood by heating the sample on a hot plate before being washed. The sample was heated to 160F, then kept between 160 – 200F for 30 minutes. The resulting biodiesel was then sampled for flash point to have a comparative measure of methanol content. Actual methanol content tests were not performed.

Approximately 3 – 5 gallons of each sample was placed in a 5 gallon complete draining cone bottom tanks with lids. The samples were then washed once with 20% v/v water. Wash water was dripped over the crude biodiesel sample – no bubbling or other agitation was used. Settling time after washing was 45 minutes, at which point the water was decanted. Any emulsion layer was also drained with the wash water.

The resulting wash water was placed in a bottom draining container in the lab and tested for soaps. Based on the soap number, a quantity of 32% HCl was added to neutralize the soaps and achieve a pH of less than 3.5. The quantity of HCl added was based on a calculation developed at Piedmont Biofuels which is equal to the amount of HCl needed to neutralize the soaps, plus an additional 50%. This calculation was developed to achieve a pH of approximately 3.5 or less and proved successful in pilot and full-scale trials. (The more traditional and probably more accurate method is to use pH probes or strips to neutralize the wash water to the appropriate pH, and measure the quantity of HCl added. This method may be used in later trials). The neutralized wash water then settled between 1 – 24 hours. The two resulting layers were separated. The bottom water layer was then neutralized to a pH of 6 – 9 using 50% sodium hydroxide solution and sent off for testing.

Results



The methanol content as measured by flash point has a significant impact on BOD and COD. This can be seen by the results from oil sample 3 in Table 2. Methanol was responsible for 66% of the BOD in the wash water, though it is actually probably much higher considering the lab methanol recovery was not completely effective, as evidenced by the flash point (the flash point of pure biodiesel is over 100C).

The removal of methanol also had a significant impact on the ability of the water to remove soaps. Comparing methanol-in and methanol-out sample 3, the soaps in the wash water are dramatically higher on the methanol-out sample - 32250 ppm compared to 7851 ppm. Methanol removal as a method of "dropping" or settling soaps has been described before, but this adds another valuable piece of data to suggest that wash efficiency is also improved by implementing methanol recovery of the biodiesel stream.

The high FOG value on sample 1 may be explained by the variability in settle time after HCl addition, as it settled for only an hour, while other samples settled overnight. Heat and settle time were not rigorously controlled in this experiment but are important factors in improving the quality of the wash water stream and should be considered in wash water systems designs.

Oil sample #	Methanol recovered (Y/N)	Flash Point (C)	Wash water quantity (ml)	Soaps (ppm)	32% HCl added (ml)	BOD	COD	FOG
1	Y	47.5	1580	6065	4.32	11000	18000	1600
2	Y	40	1300	2328	1.37	9800	16000	150
3	Y	37.5	1860	32250	27.08	33000	59000	120
3	N		1600	7851	5.67	75000	110000	84

Table 2: Results after Treatment

*Note: BOD, COD, FOG tested on the bottom (water) phase of the wash water after HCl treatment. Soaps (ppm) are the soaps in the biodiesel before washing. Flash Point (C) is the flash point in the biodiesel before washing.

Discussion and Practical Application

The strength of untreated washwater is such that it should never be discharged to a sewer authority without approval. With a BOD of 75,000 and a COD in excess of 100,000 ppm, this wastewater could not be effectively treated unless it is diluted with significant volumes of municipal influent as in the case of peak flow times.

The wash water after methanol recovery may be more acceptable to treatment authorities and a host of treatment methods can be used to reduce these concentrations further. Generally, they are classified into three categories - physical, chemical and biological treatment. With a high strength wash water that still contains significant FOG, the removal of FOG through an improved physical separation process is the preferred first step. In contrast, for a wash water similar to sample 3, other methods such as biological treatment or distillation of volatile compounds might be reasonable approaches.

If a sewer authority has excess capacity, they may consider taking one or all of the wastewater streams evaluated here. BOD is the critical and most problematic parameter. It is a simple process to calculate the excess BOD and expected cost for a permitted discharge.

Step 1: Gather Information
Determine the following values,

1. Waste BOD strength (Should be roughly 5,000 and 50,000 BOD) - C_{in}.
2. Permitted discharge volume (in gallons per batch or per day for continuous dischargers) - Q.
3. Local sewer ordinance limits on discharge (between 200 and 400 ppm BOD) - C_p.
4. Surcharge Rate ($/lb BOD) - R.
5. Determine sampling costs (between $50 and $200 per sample) - S

Step 2: Calculate Discharge Cost

Discharge cost per gallon = $(C_{in} - C_p) \cdot 8.34 \cdot 10^{-6} \cdot R + S/Q$

As an example, for a batch of waste water similar to sample 1, discharged into a municipality charging $0.21 per lb BOD and requiring a BOD and FOG test for each 10,000 gallons, at a cost of approximately $60 of sampling per batch, the cost is less than $0.03/gallon. Compare this to the $0.06 to $0.50 per gallon charged by a compost operation or commercial waste treatment facility and the extra work associated with proper handling is usually justified. This cost is likely to be less than many other discharge methods for well-treated wash water and may lead to significant cost savings.

Conclusions

Using simple acidulation with commonly available HCl, removal of the FFA and biodiesel provides a secondary stream of product for the biodiesel plant which helps reduce the impact of yield loss, and lowers BOD by removing some of the carbonaceous material from the waste water. However, even treated biodiesel wash water is far outside the typical BOD range acceptable for most POTWs, with methanol as the major contributor to BOD. Furthermore, BOD levels which are within the standards of most POTWs (200 to 300 ppm) are not achievable even after methanol recovery alone. More complete methanol recovery will certainly be more effective at improving wash water quality. Time and planning should be given to negotiations between biodiesel plants and their local POTWs to avoid costly mistakes or shutdowns. A certified professional engineer specializing in industrial wastewater should be contracted to perform the required negotiations for new dischargers or if significant changes to the wastewater generating process are being considered.

About the Authors:

Greg Austic manages Piedmont Biofuels R&A division along with Rachel Burton and has been working in the field of biodiesel for three years. He graduated from Cornell University in 2003 and joined the Piedmont team in 2006. In that time, he has successfully developed and prototyped numerous projects including heterogenous catalytic biodiesel production methods, cavitational biodiesel production, microwave reactors, wastewater acidulation and low cost product recovery techniques.

Piedmont Biofuels *produces over a million gallons a year of ASTM D6751 on spec fuel from a wide variety of feedstocks and numerous different production methods. We have experience in batch, continuous enzymatic, super critical, homogenous catalyst, acid esterification and transesterification methods for biodiesel production and are capable of full scale project delivery from feasibility study through turn-key plant delivery. The firm has a design-build division, production expertise, business planning services, laboratory services and research and development services. (*www.biofuels.coop*)*

Simon Lobdell is the owner of Chatham Environmental Consulting (CEC) and has worked in environmental engineering firms his entire career. Starting with his experience in environmental law and leading up to his work with national wastewater experts at O'Brien and Gere, Mr. Lobdell has specialized on reducing environmental impacts assocated with industrial operations. Industrial wastewater and sidestream management is a particular focus of the firm's work.

Chatham Environmental Consulting *is a specialty firm focusing on environmental projects for industrial and residential clients. The core business of the firm is assisting client decision making and negotiation for wastewater permitting as well as planning, design, and delivery of industrial operations. The firm maintains close relationships with several Professional Engineering firms and has experience spanning the breadth of environmental issues including soil, water and air protection. (*www.chathamenv.com*)*